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13. ABSTRACT (Maximum 200 words)			
A wide variety of gas-surface and electron-surface scattering experiments, supported by lattice dynamics, molecular dynamics, and scattering calculations were carried out under the auspices of this grant. These studies were motivated by a desire to understand and control surface reactions, such as surface oxidation, the technological need to characterize the physical properties of thin films and surfaces, and the desire to understand how energy and momentum are exchanged at an interface subjected to gas-surface or electron-surface collisions. Experiments involved clean, alloyed, oxidized, and stepped metallic interfaces. Surface phonon dispersion relations, and hence surface forcefields, for clean and adsorbate covered systems were determined using inelastic atom and electron scattering, providing a microscopic basis for assessing structural stability at interfaces. Major advances occurred in our understanding of the forces which are present at atomic-level steps, as well as in the area of metallic oxidation, including oxide nucleation. Synergistic effects involving electrons were shown to significantly modify metallic oxidation kinetics. Other projects dealt with alloy surface structure and stability, adsorbate negative ion resonances, dipole interactions of adsorbates, spectroscopy of frustrated low energy adsorbate vibrational modes, molecular dynamics simulations of surface vibrational dynamics, and anharmonicity in surface potentials.			

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# Dynamics of Gas-Surface Interactions

**AFOSR-F49620-93-1-0044**

**Final Technical Report for November 1, 1992 - April 30, 1996**  
**Submitted by: Steven J. Sibener**

**Department of Chemistry and The James Franck Institute  
The University of Chicago, 5640 South Ellis Avenue  
Chicago, Illinois 60637**

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## I. Extended Abstract (See cover page for short version of abstract.)

This research initiative dealt with the interaction of neutral particle, electron, and optical beams with well-characterized single crystal surfaces. These studies were motivated by a desire to understand and control surface reactions, such as surface oxidation, the technological need to characterize the physical properties of thin films and surfaces, and the desire to understand how energy and momentum are exchanged at the surface of a material when it is subjected to gas-surface collisions, electron-surface collisions, optical illumination, or chemical reaction. During the past grant period these efforts concentrated on a variety of He and electron scattering experiments which improved our understanding of clean, alloyed, oxidized, and stepped metallic interfaces. One aspect of this work aimed to determine the surface phonon dispersion relations, and hence surface forcefields, for clean and adsorbate covered systems. Such measurements provide a crucial complement to structural studies in that they quantify how surface force constants differ from those characteristic of the bulk for a given material, how these forces vary as a function of surface temperature, and how they are modified by the presence of adsorbates and interfacial defects - giving a much needed microscopic basis for assessing structural stability at interfaces. Attention was also given to elucidating which surface vibrational modes actively participate in collision induced energy exchange, and determining under which energy regimes single phonon, multi-phonon, and electron-hole pair processes are significant energy absorption mechanisms. Major advances have occurred, for example, in our understanding of the forces which are present at steps, a useful paradigm for examining the properties of extended surface defects. We have made the first in-depth measurements of the vibrational properties of a stepped metallic surface, Ni(977), including the observation of step-induced phonons. Such measurements give valuable information on metallic bonding and interface stability near extended surface defects. These experiments have also revealed that the surface forces on the terraces of stepped interfaces can differ substantially from those of the corresponding smooth (i.e., non-stepped) surface. Major advances have also occurred in the area of metallic oxidation, including oxide nucleation, structural change, and interfacial kinetic processes which have direct bearing on metallic corrosion. We have delineated the sequence of structural changes, including kinetic parameters, which occur during the initial stages of oxidation of a stepped metallic interface. These include step doubling, step singling, the formation of two different ordered oxygen overlayers, and, finally, the onset of bulk oxide formation. This complex behavior has recently been shown to be sensitive to the amount of oxygen dissolved in the sample. In other work, synergistic effects involving low fluxes of electrons which significantly modify metallic oxidation kinetics have also been quantified. With this appreciation of how electrons can influence metallic oxidation in hand, we have now reinvestigated and determined the correct low temperature oxidation kinetics for Ni(111) - including the development of kinetic models which globally fit the oxidation data with or without the presence of electrons. Work on the surface structure, chemistry, and stability of metallic alloys is also underway, with the primary goals being to investigate how interatomic forces differ between the surface and bulk regions of an intermetallic compound, how adsorbates influence these properties, and how surface structure evolves near the disordering temperature of the alloy. These issues are of high technological interest as alloy microstructure has a direct bearing on the micromechanics of these materials. Other projects have dealt with surface phonon spectroscopy of clean and oxygen covered metallic interfaces, negative ion resonances for adsorbates, dipole interactions of adsorbed molecules, spectroscopy of frustrated low energy adsorbate vibrational modes, molecular dynamics simulations of surface vibrational dynamics, and anharmonicity in surface potentials. Measurements involving elastic and inelastic helium atom scattering, inelastic electron scattering, and molecular beam reactive scattering at interfaces formed the experimental basis of this work, while in-house developed lattice dynamics, molecular dynamics, and scattering calculations supported these investigations. We are currently establishing air/electrochemical/and ultra-high-vacuum STM/AFM imaging instrumentation which will significantly augment our research capabilities in the area of atomic-level surface chemistry.

## **II. Introduction**

The scattering of atomic, molecular, and electron beams from well-characterized single crystal surfaces is proving to be an incisive method for studying the dynamics of gas-surface and electron-surface interactions. Perhaps even more importantly, scattering measurements can be used to probe the structure, surface vibrational properties, and reactivity of clean and adsorbate covered surfaces. This Final Technical Report gives an overview of the research accomplished under the auspices of AFOSR F49620-93-1-0044 during the past 3 1/2 year grant period. The scientific projects being studied in this program were motivated by a desire to understand and control heterogeneous surface chemistry, including surface oxidation, the technological need to characterize the physical properties of thin films and surfaces, and the desire to understand how energy and momentum are exchanged at the surface of a material when it is subjected to gas-surface collisions, electron-surface collisions, optical illumination, or chemical reaction. These efforts have improved our understanding of clean and adsorbate surfaces including intermetallic alloys, oxidized, and stepped metallic interfaces. Studies involving topics of high interest to the Air Force, such as interfacial metallic oxidation and corrosion reactions, played a central role in this program.

This experimental program utilized two, in many ways unique, scattering instruments which were constructed with significant DoD funding. These instruments provide incisive data on the structure, stability, and chemical reactivity of clean and adsorbate covered metallic surfaces. One is a novel high resolution (energy and momentum) neutral particle scattering apparatus which carries out single phonon inelastic as well as non-destructive diffractive scattering measurements; it currently operates with energy resolution on the order of one wavenumber (ca. 200 micro-eV). In its inelastic scattering mode this instrument can be viewed as a surface-sensitive analog to an inelastic neutron scattering spectrometer, one which provides unique information on interfacial vibrational dynamics and interfacial stability. In its elastic scattering mode, it can probe surface structure with complete "contrast" from underlying layers of the sample, providing, for example, a straightforward view of real-time surface structural changes during surface reactions and alloy ordering. The other is a combined inelastic electron scattering/molecular beam scattering instrument which provides a wealth of information on in-situ surface reaction mechanisms, the interaction of energetic reagents such as hyperkinetic oxidants with metallic interfaces, and surface vibrations. The capabilities of these two facilities complement each other in many important and useful ways. During the next grant period the data coming from these scattering laboratories will be augmented by the addition of new air, electrochemical, and UHV STM/AFM imaging instrumentation which will significantly enhance our research capabilities.

**Section III** summarizes the personnel issues associated with this grant. It has been a remarkably productive period: eight AFOSR sponsored doctoral dissertations have resulted from this program since inception. Moreover, two other (theoretical) doctoral dissertations carried out in other groups were based on projects arising from this AFOSR sponsored program. A steady stream of undergraduate researchers have also participated in these projects; most of these Chicago undergraduates have gone on to graduate work in leading US universities.

**Sections IV and V** cover the major technical accomplishments for 1992-early 1996, a grant period which was filled with discovery. Consistent with this, many manuscripts (16) were published during this time period (listed in **Section IV.2b** of this document). Major advances occurred, for example, in our understanding of the forces which are present at steps, a useful paradigm for examining the properties of extended surface defects, such as metallic bonding and interface stability near these imperfections. Major advances have also occurred in the area of metallic oxidation, including oxide nucleation, structural change, and interfacial kinetic processes which have direct bearing on metallic corrosion. For example, we have delineated the sequence of structural changes, including kinetic parameters, which occur during the initial stages of oxidation of a stepped metallic interface. These include step doubling, step singling, the formation of two different ordered oxygen overlayers, and, finally, the onset of bulk oxide formation. This complex behavior has recently been shown to be sensitive to the amount of

oxygen dissolved in the sample. In other work, synergistic effects involving low fluxes of electrons which significantly modify metallic oxidation kinetics have also been quantified. With this appreciation of how electrons can influence metallic oxidation in hand, we have now reinvestigated and determined the correct low temperature oxidation kinetics for Ni(111) - including the development of kinetic models which globally fit the oxidation data with or without the presence of electrons. Work on the surface structure, chemistry, and stability of metallic alloys is also underway, with the primary goals being to investigate how interatomic forces differ between the surface and bulk regions of an intermetallic compound, how adsorbates influence these properties, and how surface structure evolves near the disordering temperature of the alloy. These issues are of high technological interest as alloy microstructure has a direct bearing on the micromechanics of these materials. Other projects have dealt with surface phonon spectroscopy of clean and oxygen covered metallic interfaces, negative ion resonances for adsorbates, dipole interactions of adsorbed molecules, spectroscopy of frustrated low energy adsorbate vibrational modes, molecular dynamics simulations of surface vibrational dynamics, and anharmonicity in surface potentials.

During the past grant period we also contributed to AFOSR needs in Aircraft Aging/Corrosion. We presented a talk at the "Second Aging Aircraft Conference" held at Tinker AFB entitled "The Initial Stages of Metallic Oxidation", and have published a contribution in the Proceedings for that meeting. These activities are described in Section IV.4.

The scientific projects studied in this program were motivated by a desire to understand and control heterogeneous surface chemistry, including surface oxidation, the technological need to characterize the physical properties of thin films and surfaces, and the desire to understand how energy and momentum are exchanged at the surface of a material when it is subjected to gas-surface collisions, electron-surface collisions, optical illumination, or chemical reaction. The energy transfer questions being addressed here are central to a microscopic understanding of thermal accommodation, momentum accommodation (aircraft drag), and chemical adsorption.

We close this section by noting that an AASERT grant, "Surface Science Research Training" (AFOSR-F49620-93-1-0536) augmented the core grant which is the subject of this Final Technical Report.

### **III. Personnel**

Our research program has been quite successful in attracting and educating some of the best young scientific talent in the country, including undergraduates, graduate students, and postdoctoral fellows. Personnel who have worked on AFOSR sponsored projects during the past grant period are tabulated below.

#### **Graduate Students:**

Tom Pearl (U. of Chicago)  
 Ben Zion (U. of Chicago)  
 Jongin Hahm (U. of Chicago)  
 Errol Sanchez (U. of Chicago)  
 Daniel Gaspar (U. of Chicago)  
 Wenhui Liu (U. of Chicago)

Michael Stirniman (Ph.D. March 1995; now at Battelle PNNL, postdoc)  
 Licheng Niu (Ph.D. Dec. 1994; now at Applied Materials following Bell Labs postdoc)  
 Glenn Tisdale (Ph.D. Dec. 1993; now at QMAX Corp.)  
 Suzanne King (Ph.D. March 1993; now at US-EPA)  
 Daniel Koleske (Ph.D. Dec. 1991; now at NRL following IBM Yorktown Heights postdoc)  
 Barbara Gans (Ph.D. June 1990; now at Damilik Corp. following NRL postdoc)  
 Warren Menezes (Ph.D. March 1990; now at LK Technologies following Argonne postdoc)

**Other Graduate Students** (graduate students whose doctoral work in other groups was done on theoretical problems generated by our DoD funded activities):

Eric Bittner (Ph.D. Aug. 1994; U of C advisor John Light; now at U. of Texas/Austin)

Peter Knipp (Ph.D. March. 1991; U of C advisor Ugo Fano; now at Christopher Newport U.)

**Postdoctoral Fellows:**

Kevin Gibson (U. of Chicago)

Wei Li (U. of Chicago; recently became staff member at Intel)

Thomas Curtiss (now at Univ. of Utah - faculty)

Jeong Sook Ha (now at Electronics and Telecomm. Res. Institute, Korea)

**Undergraduate Research Students**

Bill Isa (undergraduate at Chicago)

Simon Liu (summer 1995 undergraduate researcher from UCLA)

Mark de Croisset (graduate student at Harvard)

Timothy Chen (medical school at U. of Indiana)

Sarah O'Conner (graduate student at CalTech)

Jason Fleischer (graduate student at MIT)

Jeanette Sperhac (graduate student at Univ. of Colorado, Boulder)

To conclude this section, we wish to emphasize that we have been quite successful in attracting qualified women and minorities to our program and hope to continue this important trend in the future. At the present time three of our group members are women. The PI fully recognizes that the future vitality of the American science enterprise will depend on the successful involvement of women and under-represented minorities at all levels of training.

**IV. Ph.D. Dissertations, Publications, Invited Presentations, Connections to DoD**

Listed below are the documents that have resulted from our AFOSR sponsored activities. Section III.1 lists the doctoral dissertations upon which much of this work is based; Section III.2 lists the manuscripts that are due to our most recent AFOSR sponsored activities, including technical synopses of these projects; Section III.3 lists the invited presentations of the PI. Several additional manuscripts will be completed during the coming year which come from the thesis and postdoctoral work of the individuals listed in sections II and III.1 of this document.

**IV.1 AFOSR Sponsored Doctoral Dissertations (Cumulative Listing)**

Yaw-Wen Yang, Inelastic Atom Surface Scattering: LiF(001), Si(001) Surface Phonons, U. of Chicago- Chemistry, June, 1988.

Warren J. C. Menezes, Inelastic Electron Scattering Study of Ni(111) Surface Phonons, U. of Chicago- Chemistry, March 1990.

Barbara Gans, The Structure and Dynamics of Cu<sub>3</sub>Au(001) Studied by Elastic and Inelastic Helium Atom Scattering, U. of Chicago- Chemistry, June 1990.

Daniel Koleske, Studies of Surface Vibrations and Structure Using Molecular Dynamics Simulations, Lattice Dynamics Calculations, and Helium Atom Scattering, U. of Chicago- Chemistry, December 1991.

Suzanne King, Helium Atom Scattering Studies of the Cu<sub>3</sub>Au(001) Surface: The Order-Disorder Transition, U. of Chicago- Chemistry, March 1993.

Glenn Tisdale, Inelastic Electron Scattering and Lattice Dynamics Study of Ordered Oxygen Layers on Ni(111), U. of Chicago- Physics, December 1993.

Licheng Niu, Localized Surface Phonons and Surface Structural Studies of Ni(977), U. of Chicago- Physics, December 1994.

Michael Stirniman, The Interaction of Oxidizing Adsorbates with the Ni(111) Surface, U. of Chicago- Chemistry, March 1995.

[Please also note that the 1991 doctoral work of Peter Knipp under the guidance of Professor U. Fano in our physics department was stimulated by our AFOSR sponsored activities. Peter's thesis title was "Phonons on Stepped Surfaces". This program also motivated the 1994 thesis work of Eric Bittner, "Quantum Theories of Energy Transfer at the Gas-Surface Interface", which was conducted under the guidance of Professor John Light of our chemistry department]

#### IV.2a AFOSR Sponsored Publications: Cumulative 1992-96

Surface Dynamics of Ordered Cu<sub>3</sub>Au(001) Studied by Elastic and Inelastic Helium Atom Scattering, Surface Science 264, 81 (1992), B. Gans, P.A. Knipp, D.D. Koleske, and S.J. Sibener.

Generation of Pseudo-Random Sequences for Use in Cross-Correlation Modulation, Rev. Sci. Instrum. 63, 1 (1992), D. D. Koleske and S.J. Sibener.

Phonons on FCC (100), (110), and (111) Surfaces using Lennard-Jones Potentials: I. Comparison between Molecular Dynamics Simulations and Slab Technique Calculations, Surface Science 268, 406 (1992), D.D. Koleske and S.J. Sibener.

Phonons on FCC (100), (110), and (111) Surfaces using Lennard-Jones Potentials: II. Temperature Dependence of Surface Phonons Studied with Molecular Dynamics, Surface Science 268, 418 (1992), D.D. Koleske and S.J. Sibener.

Molecular Dynamics Simulations of the Basal Planes of Ni and Cu Using Finnis-Sinclair Potentials, Surf. Sci. 290, 179 (1993), D.D. Koleske and S.J. Sibener.

Shape Resonance Enhancement of Vibrational Excitations for CO Chemisorbed on Ni(111) Probed Via Inelastic Electron Scattering, J. Chem. Phys. 98, 10061 (1993), Jeong Sook Ha and S.J. Sibener.

Temperature Dependence and Anharmonicity of Phonons on Ni and Cu (110) Using Molecular Dynamics Simulations, Surf. Sci. 298, 215 (1993), D.D. Koleske and S. J. Sibener.

Surface Phonon Dispersion of p(2x2)O/Ni(111), Surf. Sci. 311, 360 (1994), G. Tisdale and S.J. Sibener.

Shape Resonance Scattering as a Probe of Excited State Adsorbate Dynamics for CO Chemisorbed on Ni(111), SPIE Proceedings Vol. 2125 "Lasers Techniques for Surface Science", pp. 296-302, 1994, Jeong Sook Ha and S. J. Sibener.

Interadsorbate Interactions in the c(4x2) NO/Ni(111) System, J. Chem. Phys. 102, 4699 (1995), M.J. Stirniman, Wei Li, and S.J. Sibener.

Electron Stimulated Oxidation of Ni(111) at Low Temperature, Surface Science Letters 329, L593 (1995), Wei Li, M.J. Stirniman, and S. J. Sibener.

Inelastic Electron Scattering Study of Metallic Oxidation: Synergistic Effects Involving Electrons During the Low Temperature Oxidation of Ni(111), J. Vacuum Science and Technology A. 13, 1574 (1995), Wei Li, M.J. Stirniman, and S.J. Sibener.

Electron Stimulated Oxidation of the Ni(111) Surface: Dependence on Substrate Temperature and Incident Electron Energy, *J. Chemical Physics* **103**, 451 (1995), M.J. Stirniman, Wei Li, and S.J. Sibener.

Observation of Phonons Localized at Step Edges: A Route to Understanding Forces at Extended Surface Defects, *Science* **268**, 847 (1995), L. Niu, D.J. Gaspar, and S.J. Sibener.

Vibrational Dynamics of a Stepped Metallic Surface: Step-Edge Phonons and Terrace Softening on Ni(977), *J. Chemical Physics* **102**, 9077 (1995), L. Niu, D.D. Koleske, D.J. Gaspar, and S.J. Sibener.

Reconstruction Kinetics of a Stepped Metallic Surface: Step Doubling and Singling of Ni(977) Induced by Low Oxygen Coverage, *Surface Science - In Press* (1996), L. Niu, D.D. Koleske, D.J. Gaspar, S.F. King and S.J. Sibener.

[There was also a short contribution to the Second USAF Aging Aircraft Conference entitled "The Initial Stages of Metallic Oxidation".]

#### **IV. 2b Technical Abstracts of Completed Manuscripts: Cumulative 1992-1996**

**Surface Dynamics of Ordered Cu<sub>3</sub>Au(001) Studied by Elastic and Inelastic Helium Atom Scattering, Surface Science **264**, 81 (1992), B. Gans, P.A. Knipp, D.D. Koleske, and S.J. Sibener.**

Inelastic helium atom scattering has been used to measure the surface phonon dispersion curves for the (001) face of the ordered phase of Cu<sub>3</sub>Au along the <100> (i.e.,  $\Gamma$ -M) direction. We report the spectroscopic observation of two surface phonon modes on this fcc alloy, and present a detailed description of the scattering instrument that was used for making these measurements. The lower energy surface phonon mode, the Rayleigh wave, has an energy of 7.1 ( $\pm 0.5$ ) meV at M'. The higher lying feature is an optical mode with an energy of 12.5 ( $\pm 1.0$ ) meV, which shows little dispersion across the surface Brillouin zone. This phonon mode might be interpreted as a folded Rayleigh mode. The experimentally measured dispersion curves do not agree with those generated by a lattice dynamical slab calculation which uses a pair potential force-field that successfully models the bulk vibrations of the ordered alloy. The best fit to our experimental data indicates that the force constant between the first and second layer Cu atoms needs to be stiffened by approximately 20% with respect to the corresponding bulk value.

**Generation of Pseudo-Random Sequences for Use in Cross-Correlation Modulation, Rev. Sci. Instrum. **63**, 1 (1992), D. D. Koleske and S.J. Sibener.**

In this paper we discuss how pseudo-random sequences are generated for use in cross-correlation modulation experiments and present means for generating all pseudo-random sequences (modulo-two) that have a maximum length of  $N=2^n-1$ , with  $n=2-12$ . We explain the criteria that the pseudo-random sequences must satisfy, and find the set of recursion coefficients which are used to generate the pseudo-random sequences. These sets of recursion coefficients were calculated for  $n=2-16$ , with  $n=2-12$  being explicitly presented in this paper. We also explain how each set of recursion coefficients can be used to generate maximum length pseudo-random sequences of length sufficient for use in cross-correlation chopping.

**Phonons on FCC (100), (110), and (111) Surfaces using Lennard-Jones Potentials: I. Comparison between Molecular Dynamics Simulations and Slab Technique Calculations, Surface Science **268**, 406 (1992), D.D. Koleske and S.J. Sibener.**

The surface phonon dispersion curves have been calculated for FCC (100), (110), and (111) surfaces using molecular dynamics (MD) simulations and Lennard-Jones pair potentials. In the low temperature limit these MD simulations have been compared to the results from slab-technique lattice dynamics calculations of the type pioneered by Allen, Alldredge, and de Wette. We compare the dispersion results between these two methods as a prelude to MD studies of the dispersion curves at elevated temperatures. At temperatures where the dynamical behavior is

well described within the harmonic approximation, the two techniques should provide equal descriptions of surface phonon spectral densities and phonon frequencies. In this paper we demonstrate this agreement.

**Phonons on FCC (100), (110), and (111) Surfaces using Lennard-Jones Potentials: II. Temperature Dependence of Surface Phonons Studied with Molecular Dynamics, Surface Science 268, 418 (1992), D.D. Koleske and S.J. Sibener.**

In this paper we present temperature dependent studies of the surface phonon dispersion relations for FCC (100), (110), and (111) faces using molecular dynamics (MD) simulations and Lennard-Jones potentials. This study was conducted in order to investigate how anharmonic potential terms influence the dynamical properties of the surface. This was accomplished by examining the temperature dependence of the  $Q$ -resolved phonon spectral density function. All phonon frequencies were found to decrease linearly in  $T$  as the temperature was increased, while at low temperatures the phonon linewidths increased linearly with  $T$ . At higher temperatures, some of the phonon linewidths changed from having a linear to a quadratic dependence on  $T$ . The temperature at which this  $T$  to  $T^2$  change occurs is surface dependent and occurs at the lowest temperature on the (110) surface. The  $T^2$  dependence arises from the increasing importance of higher order phonon-phonon scattering terms. The phonons which exhibit  $T^2$  dependence tend to be modes which propagate perpendicularly or nearly perpendicularly to the direction of maximum root-mean-squared displacement (RMSD). This is especially true for the linewidth of the  $S_1$  mode at  $X$  on the (110) surface where, at  $T \approx 15-23\%$  of the melting temperature, the RMSD perpendicular to the atomic rows become larger than the RMSD normal to the surface. Our results indicate that the dynamics on the (110) surface may be significantly influenced by anharmonic potential terms at temperatures as low as 15% of the melting temperature.

**Molecular Dynamics Simulations of the Basal Planes of Ni and Cu Using Finnis-Sinclair Potentials, Surf. Sci. 290, 179 (1993) (D.D. Koleske and S.J. Sibener).**

Using MD simulations, we have calculated the surface phonon spectral density functions for the (100), (110), and (111) surfaces of Ni and Cu using Finnis-Sinclair (FS) potentials. These simulated phonon spectral densities are compared to the experimental inelastic helium atom scattering and HREELS data which are available for the three basal faces of Ni and Cu. We find that the overall shape of the calculated surface and second layer phonon spectral densities qualitatively reproduce those obtained from force constant fits, i.e. lattice dynamical modelling, of the experimental phonon dispersion data. Good agreement is also found between the calculated and experimental geometric separations between the surface and second layer for a given interface. However, on all surfaces the phonon frequencies calculated with Finnis-Sinclair potentials are lower than the experimentally measured values. The best agreement between our calculated results and the experimentally measured phonon frequencies was for the (100) and (110) surfaces, while the poorest agreement was on the (111) surfaces. From this we conclude that Finnis-Sinclair model potentials derived from bulk properties systematically underestimate the many body binding potential at the surface. This underestimation of the many body binding term is also manifested in the magnitude of the calculated surface stress. Our results indicate that the Finnis-Sinclair model potentials are quite adequate for a good qualitative and semi-quantitative description of the bonding changes at the surfaces of Ni and Cu.

**Shape Resonance Enhancement of Vibrational Excitations for CO Chemisorbed on Ni(111) Probed Via Inelastic Electron Scattering, J. Chem. Phys. 98, 10061 (1993) (Jeong Sook Ha and S.J. Sibener).**

This paper examines how the formation of a transient negative ion during the scattering of an electron from CO chemisorbed on Ni(111) can lead to significant enhancement in the probability for vibrationally inelastic scattering. We specifically report on the incident energy dependence for transient negative ion formation for a c(4x2) overlayer which contains only bridge-bonded molecules. The signature for this resonance is the energy dependence of the probability for vibrationally inelastic scattering from the CO intramolecular stretch and a CO frustrated rotation, both broadly peaking in the vicinity of 18 eV. Additional support for this

scattering mechanism comes from the monotonic rise in scattering intensity for both of these vibrational modes as the final (detector) angle moves towards the surface normal under otherwise fixed kinematic conditions. We also observe the presence of weak first overtone scattering for the CO intramolecular stretch under resonant scattering conditions. All of the aforementioned observations are consistent with the formation of a  $\tilde{\chi}$  shape resonance which is slightly lower in energy, and has a shortened lifetime, than in the gas phase. We also report dispersion measurements along the  $\langle 112 \rangle$  direction for both on-top and bridge-bonded species in a saturated ( $\sqrt{7}/2 \times \sqrt{7}/2$ ) R19.1° CO/Ni(111) overlayer which give information about intermolecular couplings in this compressed structure. Discussions are presented, including wavepacket arguments, which emphasize that the presence (or absence) of vibrational excitation in a given vibrational coordinate following negative ion formation can be used to infer important details about femtosecond nuclear coordinate evolution for the system in the excited state.

**Temperature Dependence and Anharmonicity of Phonons on Ni and Cu (110) Using Molecular Dynamics Simulations, Surf. Sci. 298, 215 (1993) (D.D. Koleske and S. J. Sibener).**

Molecular dynamics simulations were performed for Ni(110) and Cu(110) using a Finnis-Sinclair model potential. During the simulations the temperature dependencies of the mean-square displacements (MSD), the layer-by-layer stress tensors, and the surface phonon spectral densities were measured. A more pronounced increase in the MSD perpendicular to the atomic rows was observed as the temperature was increased as compared to either the other in-plane direction or along the surface normal. Also, at each temperature studied, the MSD along the direction normal to the surface were always larger in the second layer than in the first. Our calculations reveal that the surface phonon frequencies all decrease linearly with increasing temperature. Moreover, the surface phonon linewidths increase linearly with T at low T, and then exhibit an increased sensitivity to temperature variation, changing from a T to  $T^2$  dependence, approximately 150° before the onset of defect creation at the surface. These simulation results imply that the Ni(110) and Cu(110) surfaces do not extensively roughen before the onset of adatom-defect formation, and, in confirmation of experimental findings, that the rapid decrease of specular intensity for helium or electron scattering at elevated temperatures is due to the influence of anharmonicity in the surface potential.

**Surface Phonon Dispersion of p(2x2)O/Ni(111), Surf. Sci. 311, 360 (1994) (G. Tisdale and S.J. Sibener).**

Using inelastic electron scattering we have mapped the salient surface phonon features of the p(2X2)O/Ni(111) system along the  $\Gamma$ -M direction of the surface Brillouin zone. Because of the diffuse scattering properties of the system, we have developed a maximum entropy deconvolution routine in order to extract precise spectroscopic information from the data. With this routine a set of experimental dispersion curves were successfully obtained for the O/Ni system. We have additionally developed a lattice dynamical model of the system and used spectral density curves from this to produce theoretical dispersion curves for comparison to the experimentally generated curves. From these comparisons we conclude that the bonding interactions in the topmost nickel layers are well described by a scaling relation which relates intermetallic force constants and bond length, and that the various bond lengths present in the surface region can be referenced to a single force constant description of the bulk Ni-Ni interaction. The surface forcefield derived in this way for p(2X2)O/Ni(111) differs significantly from that of the clean Ni(111) interface.

**Shape Resonance Scattering as a Probe of Excited State Adsorbate Dynamics for CO Chemisorbed on Ni(111), SPIE Proceedings Vol. 2125 "Lasers Techniques for Surface Science", pp. 296-302, 1994 (Jeong Sook Ha and S. J. Sibener).**

This paper demonstrates that electronically resonant inelastic electron scattering can be used to probe the vibrational dynamics of chemisorbed species, and that the formation of a transient negative ion during scattering can lead to significant enhancement in the probability for vibrationally inelastic scattering. We specifically examine CO/Ni(111) chemisorbed in a c(4x2)

structure. Our measurements consist of the incident energy dependencies for vibrationally inelastic scattering from different adsorbate modes, as well as the final angular distributions for electrons emerging from the transiently formed resonance. We also observe the presence of weak first overtone scattering for the CO intramolecular stretch under resonant scattering conditions. All of the observations are consistent with the formation of a  $\text{f}$  shape resonance in the vicinity of 18 eV which is slightly lower in energy, and has a shortened lifetime, than in the gas phase. Discussions are presented which emphasize that the presence (or absence) of vibrational excitation in a given vibrational coordinate following negative ion formation can be used to infer important details about femtosecond nuclear coordinate evolution for the system in the excited state.

**Interadsorbate Interactions in the c(4x2) NO/Ni(111) System, J. Chem. Phys. 102, 4699 (1995) (M.J. Stirniman, Wei Li, and S.J. Sibener).**

Electron energy loss spectroscopy was used to map the dispersion of the dipole active internal NO stretch and of the NO frustrated translation, which has not been previously observed, in the c(4x2) NO/Ni(111) system. The dispersion of the dipole active mode was fit with a model that assumed electrostatic dipole-dipole coupling (including image dipoles) between the adsorbates. The frustrated translation, on the other hand, showed no dispersion to within the resolution of the experiment across the entire surface Brillouin zone of the Ni(111) substrate.

**Electron Stimulated Oxidation of Ni(111) at Low Temperature, Surface Science Letters 329, L593 (1995) (Wei Li, M.J. Stirniman, and S. J. Sibener).**

We have found that electron beams from 5 eV to 2 keV stimulate facile nickel oxide growth on Ni(111) at 120 K, and that oxidation occurs extremely slowly at low temperatures when electron irradiation is absent. These results differ significantly from previous studies, discrepancies which can be attributed to synergistic effects involving electrons. A model is proposed which quantitatively accounts for the data and yields relevant cross sections. These findings are of fundamental importance to metallic oxidation and corrosion, and may find application in electron beam and STM lithography.

**Inelastic Electron Scattering Study of Metallic Oxidation: Synergistic Effects Involving Electrons During the Low Temperature Oxidation of Ni(111), J. Vacuum Science and Technology A. 13, 1574 (1995) (Wei Li, M.J. Stirniman, and S.J. Sibener).**

Oxygen adsorption and oxide growth on Ni(111) has been investigated at 120 K by high resolution electron energy loss spectroscopy (HREELS). We have found that an electron beam can stimulate nickel oxide growth at all incident electron energies examined, spanning the range from 5 eV to 2 keV. When electron irradiation is absent, oxidation occurs extremely slowly on this surface at low temperatures, resulting in mainly chemisorbed oxygen. We demonstrate that HREELS is capable of simultaneously monitoring oxide growth and characterizing the chemical nature of the oxygen/nickel interface, providing a useful complement to our earlier Auger spectroscopy based study of electron stimulated oxidation of this interface. We propose a model for the observed effect in which electrons create oxide nucleation centers on the Ni(111) surface in the presence of chemisorbed oxygen. This model allows us to quantitatively account for the data, including extraction of the relevant cross sections.

**Electron Stimulated Oxidation of the Ni(111) Surface: Dependence on Substrate Temperature and Incident Electron Energy, J. Chemical Physics 103, 451 (1995) (M.J. Stirniman, Wei Li, and S.J. Sibener).**

The effect of surface temperature on the rate of oxidation of the Ni(111) surface with and without electron irradiation has been determined for temperatures between 120K and 340K. The oxidation rate in the presence of an electron beam demonstrates an inverse dependence on the substrate temperature, while without an electron beam we observe a decrease in oxidation rate with decreasing substrate temperature, decreasing almost to zero at 120 K. Similar rates are observed near room temperature for the two cases. We have found that oxidation of this surface can be well described by either of two rate expressions: one that relates the oxide growth rate to the rate of lateral growth of two dimensional oxide islands, and another that is first order in oxide and oxygen coverages at the surface. The physical implications of each model are discussed in

terms of the nucleation sites created by the electron beam, and the rate constants for oxidation at these nucleation sites. We present evidence that the nucleation sites created by the electron beam are metastable, with an unusually long half-life of about  $600 \pm 150$  seconds. We have also investigated the dependence of the cross section for nucleation center creation as a function of incident electron energy at constant electron flux and constant oxygen exposure. The energy dependencies of the cross section for nucleation center creation and the yield of secondary electrons produced by irradiation from the incident electron beam are compared, leading to consideration of the role that such secondary electrons may have in the creation of nucleation centers. The results presented herein delineate the correct low temperature oxidation kinetics for Ni(111) in the absence of perturbing electrons. They also provide a cautionary note for experiments which use electron-based probes, or optical probes which generate intense swarms of electrons, for studying the oxidation kinetics of metals, and perhaps other classes of interfacial reactions.

**Observation of Phonons Localized at Step Edges: A Route to Understanding Forces at Extended Surface Defects, *Science* **268**, 847 (1995) (L. Niu, D.J. Gaspar, and S.J. Sibener).**

Inelastic helium atom scattering has been used to measure the phonons on a stepped metallic crystalline surface, Ni(977). We observe two new branches of step induced phonons when the scattering plane is oriented parallel to the step edges and perpendicular to the terraces. These branches are identified as transversely polarized step localized modes which propagate along the step edge. Analysis reveals significant anisotropy in the force field near the step edge, with all forces being substantially smaller than in the bulk. Such measurements give valuable new information on metallic bonding and interface stability near extended surface defects.

**Vibrational Dynamics of a Stepped Metallic Surface: Step-Edge Phonons and Terrace Softening on Ni(977), *J. Chemical Physics* **102**, 9077 (1995) (L. Niu, D.D. Koleske, D.J. Gaspar, and S.J. Sibener).**

Inelastic helium atom scattering has been used to measure the surface and step localized phonons on a stepped metallic surface, Ni(977). These time-of-flight measurements were carried out both perpendicular and parallel to the step direction. Surface phonon dispersion data collected across the steps show backfolding of the surface Rayleigh mode, and, most importantly, dramatic softening as compared to the forces present at the smooth Ni(111) surface. This softening suggests significant relaxation perpendicular to the step edge. Single-phonon scattering data collected along the step direction reveals the presence of two new step-edge localized modes, as well as the Rayleigh mode for this direction of the crystal. The Rayleigh mode here does not exhibit the notable softening that was found for the other direction. Novel in- and out-of-phase scattering measurements, with respect to the terraces, lead us to assign the new step induced modes as the two transversely polarized vibrations which propagate along the direction of the step-edge. An analytic 1-dimensional lattice model is proposed which well represents the dispersion data for these two step modes; its use allows us to determine the effective local force field in the two transverse directions with respect to the step-edge. The findings reported herein shed new light on such topics as interface stability, crystal growth, and charge redistribution in the vicinity of well-characterized extended surface defects

**Reconstruction Kinetics of a Stepped Metallic Surface: Step Doubling and Singling of Ni(977) Induced by Low Oxygen Coverage, *Surface Science - In Press* (1996) (L. Niu, D.D. Koleske, D.J. Gaspar, S.F. King and S.J. Sibener).**

Helium atom diffraction has been used to study the reconstruction kinetics of a stepped metallic surface, Ni(977), which sequentially undergoes step-doubling and singling upon dosing with low coverages of oxygen. Over the temperature range 390 - 470 K it was found that less than 2% of a monolayer of oxygen was sufficient to transform the initially prepared single-stepped surface to a new steady state having a double-stepped structure. The thermal range over which the doubled phase exists extends to higher temperatures when more oxygen is present. At low oxygen exposures this doubled interface reverts to the single-stepped surface above 470K. Singling can also be driven by more extensive levels of oxygen adsorption. The kinetics of the step-doubling transformation which occurs below 470 K was determined to be second order with respect to single-step density, while, for temperatures above 470 K, step-singling followed first

order kinetics with respect to the double-step density. Oxygen atoms adsorbed at step edges play a crucial role in these transformations. Arrhenius analysis is used to extract energetics for the step-doubling and singling reconstructions. These results delineate the sequence of mechanistic steps which occur during the initial stages of oxidation of a stepped metallic interface which precede the onset of bulk oxidation, findings which are important for developing an improved understanding of metallic oxidation and corrosion.

#### IV.3 Invited Presentations by the PI: 1992-1996

##### 1992

Columbia University, Department of Chemistry, New York, NY  
 Indiana University, Department of Chemistry, Bloomington, IN  
 APS March Meeting, Indianapolis, IN  
 National ACS Meeting (April 1992) Symposium on Intermolecular Forces: From Simple to Complex Systems, San Francisco, CA  
 National ACS Meeting (August 1992), Organizer- Symposium on "Surface Chemistry from Reaction Dynamics Through Materials Growth", Washington, D.C.  
 University of Oregon, Eugene, Chemical Physics Institute Retreat Speaker, Coos Bay, OR  
 University of Wisconsin at Madison, ACS Lecturer in Analytical Chemistry, Madison, WI

##### 1993

University of Houston, Department of Chemistry, Houston, TX  
 Rice University, Department of Chemistry, Houston, TX  
 University of Colorado at Boulder Joint Institute for Laboratory Astrophysics - Chemical Physics Colloquium, Boulder, CO  
 Harvard University, Department of Chemistry, Cambridge, MA  
 National ACS Meeting (March, 1993) Symposium on Surface Science of Catalysis, Denver, CO  
 University of California at Santa Barbara, Department of Chemistry, Santa Barbara, CA  
 California Institute of Technology, Department of Chemistry, Pasadena, CA  
 Colorado State University, Department of Physics, Ft. Collins, CO  
 Adriatico Research Conference on Scattering From Surfaces International Centre for Theoretical Physics, Trieste, Italy  
 Gordon Research Conference on Dynamics of Gas-Surface Interactions Proctor Academy, Andover, NH  
 Surface Science and Catalysis Science Seminar, Lawrence Berkeley Lab., Berkeley, CA  
 Argonne National Laboratory, Chemistry Division Colloquium, Argonne, IL

##### 1994

OE LASE '94/SPIE Symposium on Laser Techniques for Surface Science  
 Conference Co-Chair and Speaker (January, 1994), Los Angeles, CA  
 National ACS Meeting (August 1994), Washington, D.C.  
 Symposium on Materials Research at the Crossroads of Physical and Solid State Chemistrys

##### 1995

Physical Chemistry/Chemical Physics Seminar, Penn State, State College, PA  
 APS March Meeting, San Jose, CA  
 OE LASE '95/SPIE Symposium on Laser Techniques for Surface Science  
 (July, 1995), San Diego, CA  
 American Vacuum Society/Illinois Section, Argonne National Laboratory, (Sept. 1995).

##### 1996

Symposium on Atomic and Surface Physics, Engelberg, Switzerland (Jan. 1996).  
 Experimental and Simulation Challenges in Nanostructured Materials: Mardi Gras Conference '96, Baton Rouge, LA (Feb. 1996).  
 MIT, Department of Chemistry, Cambridge, MA  
 APS March Meeting, St. Louis, MO, Division of Chemical Physics Program Chair

National ACS Meeting (March 1996), New Orleans, LA, Symposium on Bimolecular Surface Reactions (talk given by J. Colonell)  
UCLA, Department of Chemistry, Los Angeles, CA

#### **IV.4 Connections with DoD**

##### **IV.4a DoD Meeting Participation**

The PI and his group have attended several DoD meetings on the topic of corrosion and aging aircraft. For example:

- Graduate student Mike Stirniman participated in the "Joint AFOSR-AFMC/EN Aging Aircraft Conference" [Workshop on Aging Aircraft Research] that was held from 27-28 April 1993 at Georgia Tech in Atlanta, GA.
- Professor Sibener was an invited participant at the "Second Air Force Aging Aircraft Conference" that was held from 17 May to 19 May at the Oklahoma City Air Logistics Center, Tinker AFB, OK. His talk was entitled "The Initial Stages of Metallic Oxidation", and stimulated much discussion with the participants and sponsors.
- Professor Sibener was also an invited speaker at the AFOSR/URI Meeting on "Corrosion, Tribology, Lubrication, and Materials Fatigue Under Extreme Conditions" that was held from 17-18 August 1994 at the Beckman Institute at the University of Illinois/Urbana-Champaign. His presentation was entitled "The Initial Stages of Metallic Oxidation", and was presented at a much higher technical level than the overview talk presented earlier at Tinker AFB.

##### **IV.4b DoD Consulting of the PI**

The PI was a charter member of the Defense Science Study Group of the Institute for Defense Analyses. He is currently a consultant for IDA.

#### **V. Scientific Accomplishments and Highlights**

This section gives a detailed overview of the research accomplished under the auspices of the AFOSR during the past grant period.

For the past three years this experimental program has utilized two, fully operational scattering instruments that were constructed with significant DoD funding. One of these is a high resolution (energy and momentum) neutral particle scattering apparatus, see **Figures 1 and 2**, which routinely carries out single phonon inelastic as well as diffractive scattering measurements. The other laboratory houses an inelastic electron scattering instrument, see **Figures 3 and 4**, which also produces momentum-resolved inelastic scattering data. This new combined instrument gives us the capability to monitor the nascent reaction intermediates that form upon molecular adsorption (via *in situ* vibrational spectroscopy).

As stated in **Section IV.1**, the past three years have been highly productive ones for our program, with **16** papers (including in this count one submitted article) being published on a variety of topics [1-16], and others in various stages of preparation. These AFOSR funded activities fall into several categories, with the bracketed Ref. numbers pertaining to work published in the 1992-early 1996 time period:

##### **V.a Index to Topics**

- V.1 Initial Stages of Metallic Oxidation for a Stepped Interface, Ni(977): Kinetics for Step Doubling/Singling, Ordered Overlayer Formation, the Onset of Bulk Oxidation, and the Discovery that Oxidation Kinetics Depend on the Extent of Dissolved Oxygen [Refs. 16,17]**
- V.2 Electron Stimulated Oxidation of Ni(111) [Refs. 11-13]**

- V.3 Elucidation of the Correct Low Temp. Oxidation Kinetics for Ni(111) With or Without the Presence of Electrons - Including Kinetic Modelling [Ref. 13]**
- V.4 Surface Phonon Spectroscopy of Stepped Metallic Surfaces: A Route to Understanding Forces Near Extended Surface Defects [Refs. 14,15]**
- V.5 Molecular Dynamics Simulations and Lattice Dynamics Calculations of Surface Phonons and Bonding on Metallic Surfaces [Refs. 3-5,7]**
- V.6 Elastic and Inelastic He Scattering Studies of Intermetallic Alloys: Surface Forces, Temperature Dependent Surface Structure, Surface Ordering Kinetics, and Bond Anharmonicity for Cu<sub>3</sub>Au(001) [Refs. 1,18,19]**
- V.7 Inelastic Electron Scattering Studies of Ni(111) and O/Ni(111) [Ref. 8]**
- V.8 Dipole-Dipole Coupling and Low Energy "Frustrated" Vibrations Within Chemisorbed Molecular Overlays: c(4x2)-NO-Ni(111) [Ref. 10]**
- V.9 Resonantly Enhanced Inelastic Electron Scattering: A Femtosecond Probe of Adsorbate Dynamics [Refs. 6,9]**
- V.10 Instrumentation Development [Ref. 2]**

Descriptions of, and research highlights from, these projects are given below. Bracketed reference numbers pertain to published work from the 1992-early 1996 time period.

**V.1 Initial Stages of Metallic Oxidation for a Stepped Interface, Ni(977): Kinetics for Step Doubling and Singling, Ordered Overlayer Formation, the Onset of Bulk Oxidation, and the Discovery that Oxidation Kinetics Depend on the Extent of Dissolved Oxygen [Refs. 16, 17]**

Stepped (vicinal) single crystal surfaces are very informative model systems for probing the chemical, physical, and metallurgical properties of imperfect surfaces. Careful preparation of such surfaces allows one to produce samples having known crystallographic orientation and hence controlled numbers and types of interfacial defects. In this project we have focussed on the structural changes which one such vicinal surface, Ni(977), undergoes upon the adsorption of oxygen, a reaction regime which we have found to exhibit extensive structural transformations which precede the onset of bulk metallic oxidation. This study substantially extends the extant literature on how adsorbates induce structural transformations, including kinetics studies, of vicinal surfaces [20-32]. Knowledge of such adsorbate induced behavior contributes to our fundamental understanding of interface energetics and stability, central issues in our quest for a refined understanding of metallic oxidation and corrosion, surface passivation, chemical catalysis, and crystal growth. Our measurements provide benchmark data for theoretical models which seek to understand both the energetics and kinetic paths by which such transformations occur. Such knowledge may ultimately enhance our ability to tailor interfacial properties in order to minimize or retard the onset of bulk oxidation.

In our group we have in particular conducted a series of helium diffraction experiments, including time-resolved diffraction (kinetics) measurements, to examine the initial stages of oxidation on a stepped metallic surface, Ni(977) [also labelled as Ni(S)-{8(111) x 1(100)}]. This regularly stepped surface has a (111) terrace that is 8 atoms wide with step edges composed of (100) faces. We have focussed on the remarkable step-doubling and subsequent step-singling (undoubling) which is induced by adsorbed oxygen. Here the surface is transformed from one having 8 atom wide terraces and 1 atom high steps to one which has 15 atom wide terraces and 2 atom high steps. This transformation is driven by the adsorption of oxygen at the step edges. We see very strong helium diffraction from the clean Ni(977) surface. The positions and intensities of these peaks are well understood by us, having been modelled with a simple scattering calculation. Exposure of this surface to only ca. 0.05 Langmuirs of oxygen at temperatures in the

vicinity of 500 K leads to a massive structural change of the surface -- helium diffraction, as well as LEED, showed that the steps and terraces double in size under these conditions, i.e. a Ni(S)-{15(111) x 2(100)}-O surface is formed. The observed step "coalescence" requires as little as a few percent oxygen coverage, suggesting that the reconstruction must involve oxygen-step interactions. Other vibrational spectroscopic evidence supports this conclusion. Furthermore, the diffraction intensities from surfaces which consist of both Ni(977) and Ni(S)-{15(111) x 2(100)}-O regions can be related to the number of single and double steps that appear on the surface, giving us a superb system for studying domain growth and domain boundary aggregation. In a recently submitted paper [16] we examined the detailed kinetic mechanisms and energetics of these transformations, as well as the stability regimes for these reconstructions. We have now mapped out the structural changes which occur on a stepped, i.e., imperfect, metallic interface upon exposure to gas phase O<sub>2</sub>. These include step doubling, step singling, the formation of two different ordered oxygen overlayers, and, finally, the onset of bulk oxide formation. **These results delineate the sequence of mechanistic steps which occur during the initial stages of oxidation of a stepped metallic interface which precede the onset of bulk oxidation, findings which are important for developing an improved understanding of metallic oxidation and corrosion.** This work has attracted wide-spread attention, with several theory groups going after the electronic [33], structural and kinetics [34] aspects of our work.

The aforementioned phenomena are robust: three crystals over a two-year period have given similar results. Our recent focus have been in two directions: elucidating the kinetics of step-doubling and step-singling (undoubling), and determining the stability regimes of the different phases. We have discovered that the surface chemistry and stability regimes for different structures are sensitive to the extent of oxygen dissolved in the sample [17], and, hence, the oxidative history of the material. Our studies naturally break into two parts: experiments on pristine Ni samples, which utilize very low oxygen exposures, and experiments on samples which have been subjected to more extensive oxygen exposures, and at times intentionally allowed to accumulate sub-surface oxygen.

In the limit of relatively high levels of oxygen exposure, we have now demonstrated the existence of a remarkably rich series of oxygen-driven reconstructive transformations for Ni(977). For example, we have shown that the initial step-doubling transformation can be reversed by the subsequent addition of more oxygen to the system, i.e., step-singling occurs upon continuing oxygen exposure, as shown in **Figure 5**. This is a thermodynamically stable regime which we now know precedes the onset of bulk oxidation at moderate temperatures. The data shown in this figure are for a helium diffraction experiment conducted with the scattering plane aligned perpendicular to, i.e., across, the step direction. It shows about one hour of continuous-isothermal oxidation data (surface temperature, T<sub>s</sub>, held at 500K while exposing the surface to a constant O<sub>2</sub> pressure of  $4 \times 10^{-10}$  torr). At the beginning of this run, helium diffraction yields two distinct diffraction peaks, characteristic for out-of-phase (anti-Bragg) scattering from the clean single-stepped surface. As oxidation continues, one can clearly see the appearance and growth of a third diffraction peak centered between the two initially present peaks. This is the diffraction signature for the double-stepped surface under in-phase (Bragg) scattering conditions. The Y-axis in this plot is linearly proportional to time, and hence oxygen exposure. This figure clearly shows the evolution from the initially prepared clean and single-stepped surface to the double-stepped surface at low oxygen coverages and ultimately its return upon further oxygen exposure to a single-stepped structure.

In conjunction with these experiments, we have developed a new and very sensitive scattering methodology for probing surface structural issues on vicinal surfaces. Here we are employing in- and out-of-phase (i.e., Bragg and anti-Bragg) scattering with the scattering plane oriented along, i.e., parallel to, the step edges. This represents quite a departure for our structural work, which formerly employed scattering across, i.e., perpendicular to, the step edge direction. The scattering interferences between adjacent terraces allow for an unusually sensitive interrogation of double-step density and step-edge defect density. These new scattering methods have allowed us to push our investigations of surface oxidation to even lower oxygen coverages.

For samples without significant sub-surface oxygen content, it was found that less than 2% of a monolayer of oxygen was sufficient to transform the initially prepared single-stepped surface to a new steady state having a double-stepped structure; this occurred over the temperature range 390 - 470 K. The thermal range over which the doubled phase exists extends to higher temperatures when more oxygen is present. At low oxygen exposures this doubled interface reverts to the single-stepped surface above 470K. Singling can also be driven by more extensive levels of oxygen adsorption. The kinetics of the step-doubling transformation which occurs below 470 K was determined to be second order with respect to single-step density, while, for temperatures above 470 K, step-singling followed first order kinetics with respect to the double-step density. Oxygen atoms adsorbed at step edges play a crucial role in these transformations. Arrhenius analysis is used to extract energetics for the step-doubling and singling reconstructions. Figures 6 and 7 show representative second-order data for step-doubling kinetics, while Figure 8 shows the first order fits for singling kinetics at elevated temperatures.

We have also examined the singling kinetics for an oxygen-free doubled surface by burning off the adsorbed oxygen with hydrogen at a sufficiently low temperature to freeze in the doubled structure. This metastable surface promptly reverted to the singled surface at elevated temperatures with kinetics that were nearly identical to the low-oxygen exposed samples. Our initial thoughts on the nearly identical singling kinetics for the oxygen free and oxygen containing surfaces centered on the entropy contribution to the free energy of the system being dominant above 470 K. However, further exploration of the literature turned up several articles which demonstrate that oxygen dissolves into Ni around 500 K [35-38]. Moreover, Kortan and Park noted that samples with large mosaic spreads exhibited dissolution temperatures below this point [36], probably due to the higher density of grain boundaries on such surfaces. These observations lead us to speculate that the small quantities of adsorbed oxygen in this study may in fact dissolve into the bulk or selvedge region near 470 K, and lead to the identical kinetic behavior for the apparently oxygen-containing and oxygen-free samples. Furthermore, it has also been reported that the stability range for chemisorbed overlayers can depend on the amount of oxygen dissolved near the surface [37], with sub-surface oxygen tending to enhance the amount of oxygen on the surface at a given temperature and exposure. *Clearly, the chemical potential of the selvedge region can be modified by the presence of oxygen, thermodynamically influencing the partitioning between adsorbed and absorbed species.* This can account for the onset of doubling at temperatures above 470 K when higher exposures of oxygen are used, as shown in Figure 5. In contrast to this, Figure 9 shows the measured stability regime for the doubled surface at two relatively low oxygen coverages; here, without substantial dissolved oxygen in the sub-surface, the reversion to a singled stucture is completed by ca. 480 K.

These measurements complement our structural work which examined oxidation at higher exposures of oxygen [17], including more extensive levels of bulk oxidation, as well as more recent work from our group on the oxidation kinetics of Ni(111) [11-13]. They are also a part of our larger thrust, which is to understand how surface forces influence, and correlate with, surface structure and chemical reactivity. Work from our group along these lines includes surface phonon measurements on clean [39] and oxygen covered [8] Ni(111), which taken together show how oxygen adsorption can modify the surface force field on a smooth metallic interface. More recent work has moved this discussion to include vicinal (imperfect) surfaces, where surface phonon spectroscopy measurements of Ni(977) [14,15] have revealed the presence of step-induced phonon modes (as well as systematic changes in the terrace forces as compared to the (111) surface). Such modes hold the key to elucidating the binding forces present in the vicinity of low-bonding-coordination sites -- information central to the kinetic issues being addressed by our group.

The time is now clearly ripe for an STM experiment to examine the microscopic real-space and real-time dynamics of this, and other step doubling/singling systems. The ability of STM to distinguish singles and doubles is clear, as has been shown, for example, in recent work on Ni(771) [27,28], Mo(100) [31], and Pt(997) [32]. Such measurements would nicely complement the kinetic database now in hand, and would hopefully reveal additional details of how step-adsorbed oxygen influences the rate at which Ni atoms detach from the step edge and migrate

over the step region from one terrace to the next. Such experiments will be conducted with our new UHV-STM during the coming grant period. Information on the location of adsorbed oxygen as a function of coverage might also be extracted from such measurements [40]. *In situ* atomic level microscopy may also help quantify how step-edge roughness (kinks) influences the local reconstruction dynamics. Such imaging would also reveal how step meandering contributes to the doubling mechanism, i.e., whether one should view this as a "zippering" process in which one point of contact (pinning connection) between adjacent steps greatly accelerates step merging. Theoretical work along these lines using Monte Carlo simulations has recently been reported by Khare *et al.* [34]. The combination of experimental data of the type being generated by our group with Monte Carlo and molecular dynamics should moreover allow critical tests of electronic structure calculations which give values for adatom diffusion away from step edges, along step edges, and across terraces [41], as well as the importance of step meandering in the coalescence process [34,42]. In addition to STM measurements, this scattering work will be extended to other stepped metallic surfaces of Ni, Al, Pt, Ti and metallic alloys such as Cu<sub>3</sub>Au and NiAl. Surface phonon studies are also planned on the clean and oxidized surfaces of these materials which will tell us about the surface forces which are present at these interfaces (see later sections of this document). Metallic oxidation experiments employing **atomic oxygen** will then be initiated, including HREELS measurements, as discussed in later sections of this proposal; metallic alloys of high technological as well as scientific interest, such as NiAl and TiAl, will be involved in these studies.

## V.2 Electron Stimulated Oxidation of Ni(111) [Refs. 11-13]

In our electron scattering/molecular beam facility we have conducted a detailed investigation of the low and intermediate temperature oxidation/corrosion kinetics of Ni(111) [11-13]. We have found that **low fluxes of electrons can create nucleation centers which significantly accelerate the oxidation of this interface**. These findings have led to a significant revision of the literature on this topic. The synergistic effects on metallic oxidation induced by electrons have been quantified; cross-sections for this phenomenon are given in the three papers which we published on this topic in 1995. Electron irradiation either *during* oxygen exposure, or *alternating* with it, can lead to this effect, indicating that the electron beam creates nucleation centers for nickel oxide growth. Moreover, after becoming sensitized to the issue of electron effects on metallic oxidation, we have reexamined and determined the correct oxidation behavior for Ni(111) both with and without the presence of electrons [13]. Kinetic models were derived which globally fit the oxidation data, whether electrons are present or not, and, if present, for electrons spanning the range from about 30 eV-2keV with fluxes from microamps through milliamps. *In situ* vibrational spectroscopy (HREELS) has also been used to follow the transition from the initially adsorbed chemisorbed oxygen to the formation of bulk metallic oxide.

The ability of electrons to perturb experimental systems such that they deviate from their typical behavior has been well documented in the literature. One of the most obvious situations is when electron bombardment can induce damage or structural change at an interface, as has been reported for low energy electron diffraction (LEED) studies for many years [43]. More directly related to this study are instances where electrons provide a powerful method of stimulating physical and chemical effects and establishing new phenomena: electrons can stimulate desorption [44], adsorption [45], dissociation [46], migration [47], and oxidation [48,49]. These effects clearly show that electrons have the capability to modify the nascent phenomena being investigated, at times so markedly that the conclusions drawn may not be directly applicable to the unperturbed system. This project has demonstrated that this can be particularly troublesome when studying oxidation/corrosion reactions with electron based probes.

The observations which triggered our investigations are shown in **Figure 10**. Here we measured the oxygen uptake of a Ni(111) surface at 120 K and 270 K with Auger spectroscopy. Data were collected using three different procedures. In the first case (**Figure 10(a)**, solid triangles) the sample was simultaneously exposed to both oxygen and an electron beam from the Auger system's electron gun. Auger spectroscopy measurements were then performed at various exposure times in order to assess the extent of oxygen uptake by the sample. In the second case

data were obtained by first dosing the sample to the desired oxygen exposure, and then measuring the oxygen content of the sample with AES at 120 K and 270 K, **Figure 10(a)** open diamonds and squares, respectively. Then, before adsorbing oxygen to the next desired total oxygen exposure, the sample was first cleaned by sputtering and annealing. The utilization of this procedure ensured that the Ni(111) substrate was not subjected to electron irradiation at any time during oxygen exposure.

When dosing oxygen without electron irradiation at 120 K, **Figure 10(a)**, we find that following the initial chemisorption region there is very little further oxygen uptake, in contrast to earlier low temperature results [50]. Moreover, even for very long exposure times, the saturation level remains a factor of three lower than previously reported [50]. However, with electrons and oxygen simultaneously present we observe facile oxygen uptake, with a growth curve that reproduces previously reported low temperature oxygen incorporation data [50]. We also note that the growth curve at 270 K without electron irradiation agrees quantitatively with previous findings for this system. This agreement at 270 K, in spite of the presence of significant electron fluxes in the prior studies [50-52], suggests that synergistic effects involving electrons which modify the kinetics of oxidation become much less important for this interface near room temperature [13]. Our results in Figure 10(a) convincingly demonstrate that facile oxide growth at low temperature is actually an effect stimulated by electron beam irradiation, and is not an inherent characteristic of the Ni(111) interface.

Several key observations were considered in proposing a kinetic model for our results. Oxygen is known to adsorb dissociatively on Ni(111) above 20 K [53]. We have also shown that it is not necessary to simultaneously expose the target surface to both electrons and molecular oxygen in order to grow nickel oxide at 120 K, and, in fact, a single exposure of a chemisorbed oxygen overlayer to a 20 sec. dose of 2keV electrons at 2 mA/cm<sup>2</sup> is sufficient to stimulate the growth of 3 ML of oxide upon subsequent oxygen exposure. Finally, we have found that electron irradiation of the clean Ni(111) surface using similar electron energies and currents does not promote low temperature oxidation. In light of these observations, we have ruled out electron induced dissociation of chemisorbed molecular oxygen, gas phase oxygen/electron interactions, and electron beam damage of the substrate as possible mechanisms. Further, other authors have shown that similar electron exposures lead to negligible surface heating [47,48], thus ruling out thermal effects.

Starting with the above view we have developed a kinetic model which provides an excellent description of our results, based on the premise that electrons create nucleation centers around which nickel oxide islands form and grow. We assume that the number of nucleation centers, N, created by the electrons follows a differential rate law which, when integrated, yields:

$$\frac{N}{N_0} = 1 - \exp(-\phi_e \sigma t) \quad (1)$$

where  $N_0$  is the saturation number of nucleation centers,  $\phi_e$  is the electron flux density in electrons per cm<sup>2</sup> per second, t is electron exposure time, and  $\sigma$  is the (energy dependent) cross section for the creation of nucleation centers by the electron beam. These energy-dependent cross sections have been extracted from our data [13], as shown in **Figure 11**. The energy dependencies of the cross section for nucleation center creation and the yield of secondary electrons produced by irradiation from the incident electron beam are compared, leading to consideration of the role that such secondary electrons may have in the creation of nucleation centers.

Using a simple first order kinetics model, we can describe the rate of nickel oxide growth as:

$$\frac{d\theta}{dt} = k(\theta_s - \theta) \frac{N}{N_0} \quad (2)$$

where  $\theta$  is the oxygen coverage,  $\theta_s$  is saturation coverage, and  $k$  is the rate constant for oxide growth around the nucleation centers. Integrating Eqn. (2), with  $N/N_0$  given by Eqn. (1), and subject to the initial condition  $\theta = \theta_c$  at  $t = 0$ , where  $\theta_c$  is the chemisorption saturation coverage and  $t$  is the oxygen exposure time, we have:

$$\theta = \theta_s - (\theta_s - \theta_c) \exp(-k(t + \frac{1}{\phi_e \sigma} \exp(-\phi_e \sigma t) - \frac{1}{\phi_e \sigma})) \quad (3)$$

We have compared the results predicted by Eqn. (3) to experimental data collected by two complementary procedures. It successfully predicts the extent of oxide formation as a function of electron beam current density for fixed oxygen exposure. Using no adjustable parameters, it can also quantitatively reproduce the oxygen uptake data obtained as a function of exposure time taken at several fixed electron beam current densities. Figure 12 shows the excellent agreement between the predictions of our model and experimental oxygen uptake data taken with simultaneous oxygen and electron exposure using a 2 keV beam at current densities of 1.3, 9.8, and 2000  $\mu\text{A}/\text{cm}^2$ .

Work is now underway to elucidate the nature and mechanism of production of these electron induced nucleation centers. The similarity of the oxidation behavior with and without electron irradiation at room temperature suggests that the number of electron created nucleation centers is a decreasing function of temperature, and preliminary data indicates that these nucleation sites may be metastable [13]. We are also examining the role that secondary electrons may have in the creation of these nucleation centers [13]. In addition to expanding these measurements to other metals, such as Al, we are also contemplating the use of this effect to induce spatially localized regions of metallic oxide using electrons from scanning electron (SEM) and scanning tunneling (STM) microscopes. Such experiments will be attempted when our new UHV-STM facility becomes operational.

### V.3 Elucidation of the Correct Low Temp. Oxidation Kinetics for Ni(111) With or Without the Presence of Electrons - Including Kinetic Modelling [Ref. 13]

After completing our study of synergistic effects involving electrons during metallic oxidation (see previous section) we embarked on a detailed re-examination of the true oxidation kinetics of Ni(111) both in the absence of any electrons and with various controlled doses of electrons; these experiments were carried out between 120K and 340K.

The uptake of oxygen on the low temperature electron irradiated Ni(111) surface proceeds in three distinct regions. First is a rapid uptake of oxygen to an initial coverage of about 0.4 ML chemisorbed O. This initial uptake is fairly independent of temperature or the presence of electron irradiation, and can be well described by a first order dissociative adsorption rate expression [51]. This is followed by a second rapid uptake region, associated with the nucleation and growth of nickel oxide, which demonstrates an inverse dependence of the reaction rate on the substrate temperature. The third region is a very slow thickening of the saturated nickel oxide overlayer, which is also insensitive to substrate temperature in the temperature regime explored and insensitive to the presence of electron irradiation. In contrast, oxygen uptake on this surface without electron irradiation follows the same 3-step pattern, but with an opposite substrate temperature dependence on the reaction rate in the second region [13], i.e. it exhibits normal behavior for a thermally activated process. Our work has focussed on the second kinetic regime, the nucleation and growth of nickel oxide from the saturated chemisorbed overlayer to the saturation coverage of nickel oxide, both with and without electron irradiation.

As stated above, the oxidation rate in the presence of an electron beam demonstrates an inverse dependence on the substrate temperature, while without an electron beam we observe a decrease

in oxidation rate with decreasing substrate temperature, decreasing almost to zero at 120 K. Similar rates are observed near room temperature for the two cases. Oxidation of this surface can be well described by either of two rate expressions: one (somewhat limited in scope) that relates the oxide growth rate to the rate of lateral growth of two dimensional oxide islands, and another that is first order in oxide and oxygen coverages at the surface. The physical implications of each model are extensively discussed in our paper [13] in terms of the nucleation sites created by the electron beam, and the rate constants for oxidation at these nucleation sites.

Following Holloway and Hudson [51], we have assumed that the rate of disappearance of the chemisorbed oxygen is proportional to the rate of NiO formation:

$$[O_{(ads)}](\Phi) = [O]_0 \cdot \left( 1 - \frac{[NiO](\Phi) - [NiO]_0}{3 - [NiO]_0} \right) \quad (4)$$

where  $[O]_0$  is the saturation chemisorbed oxygen coverage, the equivalent of 0.4 - 0.5 NiO layers,  $[NiO]_0$  is the initial oxide coverage, and 3 layers is taken to be the saturation coverage of NiO. The model assumes that it is the formation of NiO (and the disappearance of the Ni adsorption sites) that limits the amount of chemisorbed oxygen atoms available to form more NiO, effectively making the rate expression first order in the factor  $(3 - [NiO](\Phi))$ . The measured Auger signal is then a combination of the Auger signal due to  $[O_{(ads)}](\Phi)$ , and that due to  $[NiO](\Phi)$ , and after sufficiently long exposures, the Auger signal is entirely due to the 3 layers of nickel oxide. This approach was used because Auger spectroscopy at low resolution does not distinguish between the oxygen in nickel oxide and chemisorbed oxygen. Integration of the rate expression given above yields:

$$[NiO](\Phi) + [O](\Phi) = \frac{3}{Z+1} + [O]_0 \cdot \left( \frac{3Z}{(3 - [NiO]_0)(Z+1)} \right) \quad (5)$$

where the first term is the signal due to NiO, the second term is that due to chemisorbed oxygen, and

$$Z = \frac{3 - [NiO]_0}{[NiO]_0} \exp \left( - \frac{3 [O]_0}{3 - [NiO]_0} K \Phi \right) \quad (6)$$

where  $K$  is the rate constant for oxidation.

In contrast to the island growth model, the two fitting parameters  $K$  and  $[NiO]_0$  are independent in this model. Here  $[NiO]_0$  governs the length of the oxidation induction period, i.e. the plateau following the initial chemisorption region, and  $K$  controls the slope of the oxide formation uptake curve. Experimentally, we observe that both the induction period and the rate constant  $K$  are functions of the surface temperature, both approaching the values that they have on the un-irradiated surface near room temperature. Attempts to fit the data for electron stimulated oxidation with either of these parameters fixed were unsuccessful, while non-linear least squares fits to the data with both parameters variable gave excellent fits, as shown by the solid lines in Figure 13.

A final word on the physical mechanisms underlying the two kinetic models: the first order autocatalytic rate expression makes no assumptions as to the spatial dependence of the oxide growth, but its first order kinetics could be accounted for by a number of physical mechanisms, e.g. dendritic growth of the oxide at nucleation sites or some other complex morphology. On the other hand, the island growth model begins with the rather rigid stipulation that the (already three layers thick) oxide islands grow only laterally at their edges. The actual growth mechanism is

probably closer to a combination of these two models. At higher substrate temperatures, when the nucleation site density is low, the island growth kinetic model may be more accurate, while at lower temperatures, with a high density of nucleation sites, a more complex growth model may be more accurate. During the next grant period atomic resolution and mesoscopic microscopy experiments will be a logical follow-up to these measurements.

The results obtained in this study delineate the correct low temperature oxidation kinetics for Ni(111) in the absence of perturbing electrons. They also provide a cautionary note for experiments which use electron-based probes, or optical probes which generate intense swarms of electrons, for studying the oxidation kinetics of metals, and perhaps other classes of interfacial reactions.

#### V.4 Surface Phonon Spectroscopy of Stepped Metallic Surfaces: A Route to Understanding Forces Near Extended Surface Defects [Refs. 14,15]

During the past grant period major advances have also occurred in our understanding of surface forces for stepped interfaces. These discoveries were made in our high resolution neutral particle scattering laboratory, Figures 1 & 2, and center on the surface vibrational properties of Ni(977), a stepped metallic surface. This instrument's computer controlled rotating low background detector (flight path 1.1 meters; energy resolution ca. 250  $\mu$ eV; background level at mass 4 ca. 1-10 Hz), operating in conjunction with an intense, temperature tunable high Mach number supersonic He nozzle source (de Broglie wavelength readily tunable in the vicinity of 1  $\text{\AA}$ ), makes this an ideal facility for such single-phonon scattering studies. One can view these inelastic He scattering measurements as a surface sensitive analog to inelastic neutron scattering, which has been a remarkably successful technique for examining forces in bulk matter.

In this study we have focussed on determining the surface phonon dispersion relations, and hence surface forcefields, for a vicinal surface which contains a significant population of well-defined atomic level steps, Ni(977) [14,15]. The measurement of phonons on stepped surfaces can conceptually be divided into two categories: (i) the study of step induced phonons, which provide information on local forces at steps, and (ii) surface phonon measurements which yield information about the effect of steps on the neighboring terrace atoms. Such measurements provide much needed information for assessing, at the microscopic level, the structural stability of defect containing interfaces; they also provide us with a useful paradigm for examining the properties of extended surface defects.

These time-of-flight measurements were carried out both perpendicular and parallel to the step direction. Surface phonon dispersion data collected across the steps show backfolding of the surface Rayleigh mode, and, most importantly, dramatic softening as compared to the forces present at the smooth Ni(111) surface. Figure 14 shows a series of time-of-flight spectra taken across the steps using out-of-phase scattering conditions, while Figure 15 shows a comparison of the surface Rayleigh wave for Ni(977) in this direction with our previous results [39] for Ni(111). *One should especially note that the Rayleigh mode of Ni(977) is appreciably softened as compared to that of the Ni(111) surface.* This softening suggests significant force constant relaxation (about 32%) perpendicular to the step edge as compared to the bulk value for Ni.

Single-phonon scattering data collected along the step direction reveals the presence of two new step-edge localized modes, as well as the Rayleigh mode for this direction of the crystal. The Rayleigh mode here does not exhibit the notable softening that was found for the other direction. Novel in- and out-of-phase scattering measurements [14,15] with respect to the terraces lead us to assign the new step induced modes as the two transversely polarized vibrations which propagate along the direction of the step-edge, shown schematically in Figure 16. Figure 17 shows the dispersion curves for this direction of the crystal. Two new step edge induced modes, labelled as E1 and E2 in this figure, are clearly visible. Confirmation that E1 and E2 are step edge related came from several experiments. The most compelling of these was the observation that the adsorption of small amounts of oxygen (which is known from our previous kinetics work to migrate to the step edge) effectively quenched the scattering from these modes, but left the Rayleigh mode scattering largely unaffected, Figure 18.

Analysis reveals significant anisotropy in the force field near the step edge, with all forces being substantially smaller than in the bulk, **Figure 19**. An analytic 1-dimensional lattice model was developed which well represents the dispersion data for these two step modes; its use allowed us to determine the effective local force field in the two transverse directions with respect to the step-edge [15]. *Ab initio* and molecular dynamics calculations are now needed to further leverage these data. One should also note that the new and very powerful scattering methodologies introduced in this work involving in- and out-of-phase scattering conditions will be of general future use in studying the surface forcefields of clean and adsorbate covered surfaces.

During the next grant period these measurements will be extended to other stepped surfaces of clean, adsorbate covered, and alloy surfaces. Work is currently underway investigating how oxygen and nitric oxide adsorption at step edges modify metallic bonding at low coordination sites such as step edges. This work will also attempt to delineate how one-dimensional chains of molecules interact with each other when adsorbed at step edges. Such phonon experiments nicely complement the structural work on step reconstruction and adsorbate-driven doubling discussed earlier in this proposal. Our overall goal here will be to obtain [in conjunction with electronic structure calculations, molecular dynamics simulations, and further structural measurements] a detailed understanding of how step discontinuities and the presence of adsorbates influence the stability of metallic interfaces.

#### V.5 Molecular Dynamics Simulations and Lattice Dynamics Calculations of Surface Phonons and Bonding on Metallic Surfaces [Refs. 3-5, 7]

In support of our structural and inelastic scattering program, we have established in-house capabilities in lattice dynamics and molecular dynamics simulations. The lattice dynamics calculations allow us to calculate surface phonon dispersion curves at zero temperature, while the molecular dynamics simulations are important as they allow surface dynamics to be examined at finite temperature. The surface vibrational information generated in these calculations can also be used as input to quantum scattering calculations which seek to model our inelastic electron and/or helium scattering experiments. Early examples from our AFOSR supported program of such feedback between experiment and calculation are our work on Ni(111), O/Ni(111), Cu<sub>3</sub>Au(001), stepped metallic surfaces, and anharmonic effects in surface bonding. The performance of our MD code was initially verified by comparing the surface phonon dispersion curves calculated at low temperatures, using Lennard-Jones potentials, with those derived from a slab-technique lattice dynamics calculation. At temperatures where the dynamical behavior is well described within the harmonic approximation, the two techniques generate, as expected, give identical results [3].

The MD code has been used to examine anharmonic effects at elevated temperatures, initially using Lennard-Jones model potentials [4], followed by more realistic work with Finnis-Sinclair potentials [5,7]. For example, we have calculated the surface phonon spectral density functions for the (100), (110), and (111) surfaces of Ni and Cu using Finnis-Sinclair (FS) potentials. These simulated phonon spectral densities were compared to the experimental inelastic helium atom scattering and HREELS data which are available for the three basal faces of Ni and Cu. We found that the overall shape of the calculated surface and second layer phonon spectral densities qualitatively reproduce those obtained from force constant fits, i.e. lattice dynamical modelling, of the experimental phonon dispersion data. Good agreement was also found between the calculated and experimental geometric separations between the surface and second layer for a given interface. However, on all surfaces the phonon frequencies calculated with Finnis-Sinclair potentials were lower than the experimentally measured values. The best agreement between our calculated results and the experimentally measured phonon frequencies was for the (100) and (110) surfaces, while the poorest agreement was on the (111) surfaces. From this we conclude that Finnis-Sinclair model potentials derived from bulk properties systematically underestimate the many body binding potential at the surface. This underestimation of the many body binding term is also manifested in the magnitude of the calculated surface stress. Our results indicate that the Finnis-Sinclair model potentials are quite adequate for a good qualitative and semi-quantitative description of the bonding changes at the surfaces of Ni and Cu.

Next, we critically assessed, again using Finnis-Sinclair potentials, the temperature dependence of the calculated surface phonon spectra for Ni and Cu (110) [7]. From the simulations we extracted the temperature dependencies of the mean-square displacements (MSD), the layer-by-layer stress tensors, and the surface phonon spectral densities. A more pronounced increase in the MSD perpendicular to the atomic rows was observed as the temperature was increased as compared to either the other in-plane direction or along the surface normal. Our calculations reveal that the surface phonon frequencies all decrease linearly with increasing temperature. Moreover, the surface phonon linewidths increase linearly with T at low T, and then exhibit an increased sensitivity to temperature variation, changing from a T to  $T^2$  dependence, approximately 150° before the onset of defect creation at the surface. These MD results emphasize the important role that anharmonicity plays in the dynamics of these surfaces at elevated temperatures, in agreement with HREELS [54,55] and He scattering experiments [56] on these systems. In particular, they imply that the Ni(110) and Cu(110) surfaces do not extensively roughen before the onset of adatom-defect formation, and, in confirmation of experimental findings [56], that the rapid decrease of specular intensity for helium or electron scattering at elevated temperatures is due to the influence of anharmonicity in the surface potential.

In the future we will continue to use our in-house developed lattice dynamics, MD, and quantum scattering codes to both support ongoing experimental work in our scattering and STM programs, as well as to help survey in advance promising new systems for experimental investigation.

#### V.6 Elastic and Inelastic He Scattering Studies of Intermetallic Alloys: Surface Forces, Temperature Dependent Surface Structure, Surface Ordering Kinetics, and Bond Anharmonicity for Cu<sub>3</sub>Au(001) [Refs. 1,18,19]

We are continuing our examination of the chemical and physical properties of metallic alloy surfaces. Such studies are important to the design of material interfaces which maintain good structural properties in corrosive and especially high temperature environments. To date, there have been only a few surface studies of intermetallic compounds which comprise ordering binary alloys. A<sub>3</sub>B intermetallic compounds often form fcc lattices of which a simple cubic sublattice consists solely of minority atoms. These are interesting because they exhibit high strength even at elevated temperatures. Samples consisting of both ordered and disordered regions are of further interest, as their physical properties, such as resistance to dislocation propagation and brittleness, can be optimized for a specific application given our present understanding of the relationship between microstructure and micromechanics. For this reason 'superalloys' are currently used in high performance applications of the aerospace industry. These alloys exhibit increased hardness in their ordered phase as compared to their disordered phase or their single metal constituents.

In our group we have initially focussed on the model system Cu<sub>3</sub>Au(001), with two of the primary goals being to investigate how interatomic forces differ between the surface and bulk regions of an intermetallic compound [1,19], and how the surface structure changes in the vicinity of the disordering temperature of the alloy [18] -- ideally revealing how the ordered and substitutionally disordered surface domains evolve as a function of temperature. We have employed both elastic (for diffraction) and inelastic (for surface vibrational studies) helium atom scattering to characterize the structure and vibrational properties of Cu<sub>3</sub>Au(001). Neutral helium atom scattering is especially well suited for this study since it has extreme sensitivity to the outermost layer of the alloy; i.e., it offers a high degree of "contrast" between the surface and the selvedge region. Cu<sub>3</sub>Au(001) exhibits a high degree of long range order, with the surface existing as a c(2x2) structure. Planes perpendicular to the (001) direction consist of alternating layers of either 50% Cu-50% Au or 100% Cu composition. The low energy ion scattering study (LEIS) of Buck and Wheatly [57] has shown that the (001) surface of the ordered phase terminates exclusively with a layer consisting of 50% Cu-50% Au composition, ordered in a c(2x2) arrangement. Cu<sub>3</sub>Au is particularly interesting because the bulk undergoes a *first order* phase transition ( $T_c=663$  K) to form a substitutionally disordered phase at a temperature well

below its melting temperature ( $T_m=1226$  K). Recent theory [58] and experimental work [59,60] on the order-disorder transition at the (001) surface indicates that the transition may occur *continuously*. Although the symmetry is reduced when going from the ordered state to the disordered state, the material maintains an fcc lattice--in contrast to a surface melting transition. Because of this the structural and vibrational properties both above and below the transition temperature can be investigated in the same way.

The phonon work on the ordered phase is complete [1]. Inelastic helium atom scattering has been used to measure the surface phonon dispersion curves for the (001) face of the ordered phase of Cu<sub>3</sub>Au along the <100> direction. We have spectroscopically observed two surface phonon modes on this fcc alloy, a Rayleigh wave and a higher lying optical mode which shows little dispersion across the surface Brillouin zone. (This phonon mode may also be interpreted as a folded Rayleigh mode.) The experimentally measured dispersion curves do not agree with those generated by a lattice dynamical slab calculation which uses a pair potential force-field that successfully models the bulk vibrations of the ordered alloy. The best fit to our experimental data indicates that the force constant between the first and second layer Cu atoms needs to be stiffened by approximately 20% with respect to the corresponding bulk value.

Our main focus is presently on structural and dynamical issues at elevated temperatures in the vicinity of the bulk critical temperature, 664 K. We have seen that the surface begins to disorder at temperatures well below the bulk  $T_c$ , in agreement with previous LEED studies on this interface. We have now conducted *kinetic measurements* in an attempt to observe in real time how the surface orders following quenching from above  $T_c$  to temperatures below  $T_c$ . Our preliminary results have revealed for shallow temperature quenches that the surface orders much more rapidly than the bulk, while for deeper quenches the surface ordering rate is quite comparable to that found in x-ray studies of the bulk. The data shown in Figure 20 demonstrates such rapid ordering for a shallow quench which occurs in minutes while similar data for the bulk (from x-ray measurements [61]) take hours to order. Such dynamical measurements reveal important details about the approach to equilibrium. Higher resolution studies on this surface, and in the next grant period on other interfacial systems, will hopefully reveal how quenched systems evolve through the various stages of nucleation, ordering, and coarsening. In particular, these experiments are examining how order is established in intermetallic alloys below their critical temperatures: the temperature history of the quenched sample may strongly influence whether order is first established at the surface and propagates into the bulk, i.e., with the surface acting as a template, or whether order originates throughout the bulk of the sample. This may ultimately influence the microstructure, and hence micromechanics, of the alloy.

Anharmonic effects in the surface phonon spectrum of this surface have been observed approximately 20 degrees below the bulk  $T_c$ . Figure 21 shows the onset of increased multiphonon scattering near 647 K, an increase which we attribute to the onset of anharmonic effects in the phonon dynamics. Note that this onset coincides with the beginning of surface disordering for this alloy. Related anharmonic effects have been observed just below  $T_c$  for the bulk using neutron scattering as the dynamical probe [62]. More phonon measurements in conjunction with accurate MD simulations are needed to pursue this fascinating topic.

STM measurements are planned during the next grant period which will examine the local structural behavior of this interface at elevated temperatures. Phonon work on the oxygen covered Cu<sub>3</sub>Au(110) surface may also be considered; recent ion scattering and LEED work demonstrates a massive reconstruction for this interface upon oxygen adsorption [63]. Moreover, work on other alloy surfaces, probably beginning with NiAl(110), is anticipated. The NiAl(110) interface is particularly intriguing as recent studies suggest that hydrogen adsorption [64] removes the well-documented structural rumpling [65] of this surface.

## V.7 Inelastic Electron Scattering Studies of Ni(111) and O/Ni(111) [Ref. 8]

One of the central concerns in surface science today is to ascertain how the properties (static and dynamic) of surfaces differ from those of bulk matter. A very direct way to explore the dynamical aspects of this problem is to study the interatomic force constants in the vicinity of a surface. Several years ago we began our efforts in this area by examining the surface dynamical properties of clean Ni(111) by high resolution electron energy loss spectroscopy (HREELS) operating at high incident energies. The experimental results were analyzed using lattice dynamical and quantum multiple-scattering calculations. Our results [39,66] demonstrated that the surface force field for Ni(111) differs from expectations based upon simple extrapolation from bulk behavior. The intraplanar surface force constant is approximately 11% softer than in bulk nickel. In addition, tensile surface stress is present at the (relatively low) level of +1.6 N/m, indicating that the surface atoms have a desire to be more closely spaced than in the bulk. This level of stress has been predicted theoretically for a number of metal surfaces. These surface force field assignments were derived from lattice dynamical fits to the spectroscopic results, and were independently confirmed by quantum multiple scattering calculations. Effective medium electronic structure calculations support our major conclusions from this study [67].

During the past grant period our experimental focus was on O/Ni(111) [8], with the goal here being to see how the initial stages of oxidation modify the surface force constants of the Ni surface. Using inelastic electron scattering we have mapped the salient surface phonon features of the p(2X2)O/Ni(111) system along the  $\Gamma$ -M direction of the surface Brillouin zone. Because of the diffuse scattering properties of the system, we needed to develop a maximum entropy deconvolution routine in order to extract precise spectroscopic information from the data. With this routine a set of experimental dispersion curves were successfully obtained for the O/Ni system. We have additionally developed a lattice dynamical model of the system and used spectral density curves from this to produce theoretical dispersion curves for comparison to the experimentally generated curves. From these comparisons we conclude that the bonding interactions in the topmost nickel layers are well described by a scaling relation which relates intermetallic force constants and bond length, and that the various bond lengths present in the surface region can be referenced to a single force constant description of the bulk Ni-Ni interaction. The surface forcefield derived in this way for p(2X2)O/Ni(111) differs significantly from that of the clean Ni(111) interface. Such information is most useful in assessing how oxygen adsorption influences the structural stability of a metallic interface.

Such measurements will continue during the next grant period, being extended to include metallic overlayers, and other adsorbates, as discussed in part in the next section. We are also working on extracting information on the forces present in the *second layer* of the solid. At particular incident energies and angles we can substantially enhance the inelastic scattering arising from second layer vibrations; extant scattering theory and effective medium calculations give us guidance in these experiments.

#### **V.8 Dipole-Dipole Coupling and Low Energy "Frustrated" Vibrations Within Chemisorbed Molecular Overlays: c(4x2)-NO-Ni(111) [Ref. 10]**

Another aspect of our surface chemistry and dynamics program is to quantify the forces within adsorbed layers. The formation of ordered overayers of adsorbates implies the existence of interadsorbate interactions. These interadsorbate interactions have attracted a great deal of study over the past 20 years in attempts to gain insight into the nature of the surface chemical bond. For example, comparison of the differing adsorption geometries of NO on Pt(111), Pd(111) and Ni(111) has shown that while NO forms a high coverage 0.5ML ordered c(4x2) structure on Ni(111) at room temperature, on the Pt(111) surface NO adsorbs in a disordered fashion above 0.25ML [68], and on Pd(111) it also forms a 0.5ML c(4x2) structure, but can go on to form a higher coverage 0.75ML (2x2) structure[68,69]. This has underlined the need for further study of the intermolecular interactions in such systems. Prior work from our group centered on the low-energy frustrated vibrations of CO/Ni(111) [70].

During the past grant period we turned our focus to the interadsorbate interactions present within the c(4x2) NO/Ni(111) system. In these electron scattering experiments we successfully determined the extent of dipole-dipole coupling within the 2-dimensional NO overlayer, as well

as the frequency for the previously undetected frustrated translation (i.e., low energy libration) of NO chemisorbed on Ni(111) [10]. Such information on the low energy frustrated modes of adsorbates is important (but currently quite scarce) as they are among the first vibrational modes of the system to become thermally excited at elevated temperatures; diffusion and desorption dynamics depend critically on the frequencies of these modes.

Specifically, electron energy loss spectroscopy was used to map the dispersion of the dipole active internal NO stretch as well as the NO frustrated translation, which had not been previously observed. The dispersion of the dipole active mode was fit with a model that assumed electrostatic dipole-dipole coupling [71] (including image dipoles [72]) between the adsorbates, Figure 22. In this model, the frequency shift as a function of the momentum transfer parallel to the surface ( $\mathbf{k}$ ) is given by:

$$\frac{\omega^2(\mathbf{k})}{\omega_0^2} = 1 + \frac{\alpha_v \Sigma(\mathbf{k})}{1 + \alpha_e \Sigma(\mathbf{k})}$$

where  $\omega_0$  is the stretching frequency in the absence of dipole coupling, and  $\alpha_e$  and  $\alpha_v$  are the electronic and vibrational polarizabilities respectively.  $\Sigma(\mathbf{k})$  is the dipole sum for the interacting overlayer. Here we see that the dispersion was quantitatively fit with this model, yielding adsorbate polarizabilities; these measurements also allowed us to conveniently determine the so-called singleton frequency for this system, i.e., the reference frequency with the same static chemical environment as in the overlayer but without the effect of dipole coupling. The work on low energy frustrated vibrations led to the observation of a new vibrational mode for NO adsorbed on Ni(111). The dispersionless behavior of this frustrated translation, and the close 2.87 Å nearest neighbor distance of NO in the c(4x2) overlayer, indicate that Pauli repulsion of overlapping molecular orbitals may not be the main contributor to the dispersion of these modes.

These measurements will be extended during the coming grant period to include adsorption on vicinal surfaces. One intriguing aspect of such experiments would be the observation of low energy collective vibrations associated with molecules bound at step edges. Dispersion measurements along the step direction would presumably yield information on how molecules adsorbed in nearly one-dimensional configurations interact with each other. Low temperature inelastic scattering work on much larger molecules, such as passivating LB films and self-assembled systems, may also be attempted in order to ascertain the cohesive forces in these overlayers. This work, due to severe resolution requirements, will be carried out in our He scattering laboratory.

### V.9 Resonantly Enhanced Inelastic Electron Scattering: A Femtosecond Probe of Adsorbate Dynamics [Refs. 6,9]

We have utilized resonantly enhanced inelastic electron scattering to study the dynamical properties of chemisorbed molecules. The classic review articles of George Schulz [73,74] provide a rather remarkable tutorial on the origin and characteristics of such "temporary negative ions" in the gas phase. These articles, and the work referenced therein, provide a solid framework for initiating studies of adsorbed species. One of the great hopes here is that such studies will enable us to probe the short-time dynamics of transiently bound negative-ions on surfaces which were formed by the injection of an incident electron into a shape resonance of the molecule. Another hope is that electrons scattering by such resonant processes will be able to couple with normally forbidden spectroscopic transitions, yielding new information on the normal modes for adsorbed species.

Using this technique, we have examined how the formation of a transient negative ion during the scattering of an electron from CO chemisorbed on Ni(111) can lead to significant enhancement in the probability for vibrationally inelastic scattering [6,9]. We have determined the incident energy dependence for transient negative ion formation for a c(4x2) overlayer which contains only bridge-bonded molecules. The signature for this resonance is the energy dependence of the probability for vibrationally inelastic scattering from the CO intramolecular stretch and a CO

frustrated rotation, both broadly peaking in the vicinity of 18 eV. Additional support for this scattering mechanism comes from the monotonic rise in scattering intensity for both of these vibrational modes as the final (detector) angle moves towards the surface normal under otherwise fixed kinematic conditions. We also observe the presence of weak first overtone scattering for the CO intramolecular stretch under resonant scattering conditions. All of the aforementioned observations are consistent with the formation of a  $\Sigma$  shape resonance which is slightly lower in energy, and has a shortened lifetime, than in the gas phase. We also report dispersion measurements along the  $\langle 112 \rangle$  direction for both on-top and bridge-bonded species in a saturated ( $\sqrt{7}/2 \times \sqrt{7}/2$ ) R19.1° CO/Ni(111) overlayer which give information about intermolecular couplings in this compressed structure. Using wavepacket formulation of the dynamics we argue that the presence (or absence) of vibrational excitation in a given vibrational coordinate following negative ion formation can be used to infer important details about femtosecond nuclear coordinate evolution for the system in the excited state [75]. Our observation of a frustrated rotation seems to imply that the molecule starts to bend over in the negative ion state, possibly due to attraction of its image. One should note that our observations are the complement to electron induced desorption experiments which proceed via stimulated adsorbate rotation [76]. They also add new supporting information for surface photochemistry experiments which, in many instances, actually proceed via electron attachment

In the future one of the main goals will be to find systems which live long enough to reveal finite but truncated overtone progressions with respect to gas phase behavior. Such overtone progressions will be able to serve as clocks for the excited state lifetimes when combined with wavepacket calculations [75]. Preliminary searches in our laboratory have found just the first overtone for the CO stretch, implying an exceedingly short existence for the negative ion in this instance. Recent theoretical work suggests that longer lived excited states should indeed exist and be experimentally accessible [77]. Experiments on NO and NH<sub>3</sub> are being considered in this arena.

#### V.10 Instrumentation Development [Ref. 2]

The work described in this document was in the past grant period centered in our two fully operational scattering laboratories: one housing a rather unique high energy and momentum resolution neutral particle scattering instrument, **Figures 1 and 2**, and the other being a combined molecular beam-inelastic electron scattering instrument, **Figures 3 and 4**. Development in these two laboratories is now driven by the needs of specific experiments. For example, some phonon experiments require a more sensitive time-of-flight capability; this led us to develop methods of computing and implementing pseudo-random (cross-correlation) choppers of varying resolution capabilities [2]. A chopper with both cross-correlation and conventional short-pulse modulation patterns has now been installed in our neutral particle scattering instrument.

During the next grant period we plan to construct an RF plasma beam source for use in both scattering laboratories. This beam source will allow us to expand our studies of surface oxidation to include highly energetic oxidants. We would especially like to construct an atomic oxygen beam source for studies involving excited oxidants, such as O(<sup>3</sup>P), O(<sup>1</sup>D), and O<sub>2</sub>(<sup>1</sup>Δ). Such a plasma beam source was originally developed by the PI for work in gas phase kinetics [78], **Figure 23**, and has been successfully duplicated by other groups over the past decade. Modern broad-band RF electronics should allow it to run even more efficiently than in the past. It will be a superb addition to our studies of surface oxidation kinetics.

Finally, the major building effort for the coming grant period (now well underway) is to construct a new UHV-STM facility, shown schematically in **Figure 24**. The UHV chamber (design completed and construction underway) will house such capabilities as LEED, Auger, XPS, UPS, RGA, and STM (the XPS and UPS instrumentation will be transferred from another instrument in our group). The system will initially be based on a modified "micro-STM" from Omicron Corporation. We have taken delivery of this very compact and vibrationally isolated STM. Initial UHV-STM experiments should hopefully be launched in late summer, 1996.

## V.b References

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### V.c Figure Captions and Figures

**Figure 1.** Schematic diagram of the high resolution neutral particle scattering apparatus.

**Figure 2.** Photograph of the high resolution neutral particle scattering apparatus. To the left is the triply-differentially pumped neutral particle molecular beamline, the center chamber houses the crystal manipulator and surface diagnostic/preparation instruments, and the computer controlled rotating 2-ton detector assembly is on the right. This instrument currently generates angle-resolved (i.e., wavevector resolved) time-of-flight data with ca. 250  $\mu$ eV energy resolution.

**Figure 3.** Schematic diagram of the combined molecular beam/inelastic electron scattering apparatus. The UHV chamber has a large rotating lid which transports the (off-center mounted) manipulator to various experimental positions. Level one is for scattering and HREELS measurements (electron optics shown 90° rotated from actual orientation for presentation purposes), while Level 2 is for electron irradiation and surface preparation. The triply-differentially pumped molecular beamline has a heated supersonic nozzle beam source which is skimmed before entering the beam modulation chamber; short-pulse time-of-flight, square-wave (50% duty cycle) chopping, and cross-correlation modulation patterns are available.

**Figure 4.** Photograph of the inelastic electron scattering instrument.

**Figure 5.** Structural evolution of Ni(977) surface while dosing with  $4 \times 10^{-10}$  torr of oxygen at a crystal temperature of 500K. There are 40 sequential helium diffraction runs, with each run taking 40 sec. Scattering is across the steps in the "downstairs" direction ( $\theta_i=30.4^\circ$ ,  $E_i=20.7$  meV) with  $\theta_i$  measured from the terrace normal.

**Figure 6.** Step-doubling as a function of oxygen coverage at a crystal temperature of 450K: (a) Raw data with fits to second order kinetics; (b) Rate constant obtained from fits; (c) Initial doubling rate. Both rates levels off at about 0.012ML of oxygen.  $\theta_i=33.4^\circ$ ,  $E_i=22.0$  meV.

**Figure 7.** Step doubling: (a) Fits of second order kinetics to the double step diffraction intensities as a function of time at different crystal temperatures with 0.0096ML oxygen; (b) Arrhenius analysis of the process (see elaboration in text);  $E_a=0.52\pm 0.03$  eV,  $A_0 = 10^{3.1\pm 0.3}$   $s^{-1}$ .  $\theta_i=33.4^\circ$ ,  $E_i=22.0$  meV.

**Figure 8.** Step-singling with oxygen. (a) First order kinetic fits to the decay of double-step diffraction intensities as a function of time at different crystal temperatures with 0.0096ML oxygen. (b) Arrhenius analysis of the data.  $\theta_i=33.4^\circ$ ,  $E_i=22.0$  meV.

**Figure 9.** Diffraction intensities (linearly proportional to the double step population) as a function of crystal temperature 40 minutes after oxygen dosing. (a)  $[O] = 0.0036$  ML. (b)  $[O] = 0.0096$  ML.

**Figure 10.** Oxygen uptake vs. oxygen exposure under various experimental conditions. (a) Solid triangles: Oxygen uptake during simultaneous exposure of the surface to both electrons and oxygen at 120 K; Open diamonds and squares: Oxygen uptake without electron exposure at two 120 K and 270 K; (b) Oxygen uptake vs. oxygen exposure with the sample at 120 K and simultaneously (solid triangles) or alternately (open circles) exposed to electrons and oxygen. Electron beam parameters:  $E_i = 2$  keV,  $I = 2$  mA/cm<sup>2</sup>.

**Figure 11.** Dependence of the cross section for the creation of nucleation centers on the energy of the incident electron beam (solid circles). The solid line is a curve drawn to guide the eye. The open squares are data for the number of secondary electrons emitted from polycrystalline evaporated nickel films per incident primary electron ( $\delta$ ) as a function of primary electron energy (from D.E. Woolridge, Phys. Rev. B 56 (1939) 1063.).

**Figure 12.** Oxide growth vs. time for three different electron beam current densities with the sample at 120 K,  $E_i = 2$  keV and  $P_{Ox} = 3 \times 10^{-8}$  Torr. Solid lines are calculations generated from Eqn. (3).

**Figure 13.** Oxygen uptake vs. exposure data showing non-linear least squares fits using the autocatalytic kinetic model (Eqn. 5 of Section VI.3).

**Figure 14.** The surface Rayleigh mode measured using out-of-phase conditions in the scattering plane perpendicular to the steps. Panel (a) shows a typical group of time-of-flight spectra. Panel (b) shows the same data with time converted to energy transfer. Panel (c) shows the data plotted as energy transfer vs momentum exchange. The solid lines are the scan curves, i.e., the energy-momentum acceptance conditions of the detector for various scattering conditions. The other (apparent) inelastic feature in the lowest spectrum is actually an artifact, called a decepton, which is diffracted elastic flux coming from the finite energy spread of the incident helium beam.

**Figure 15.** All of the data taken with scattering plane perpendicular to the steps and using out-of-phase conditions. Panel (a) shows energy transfer vs momentum exchange and panel (b) shows the folded zone phonon dispersion curve.

**Figure 16.** The Ni(977) surface and polarization directions for the step-induced phonon modes.

**Figure 17.** Panel (a) shows energy transfer vs momentum transfer for the  $E_1$ ,  $E_2$ , and Rayleigh modes. The solid lines are the corresponding surface Rayleigh mode of Ni(111). Open symbols are for data taken using in-phase conditions, filled symbols for data taken using out-of-phase conditions. Circles correspond to the Rayleigh mode, triangles to the new modes. Panel (b) shows the same data folded into the first surface Brillouin zone.

**Figure 18.** Adsorbate effects on the two new modes. Left side is in-phase data: Panel (a) is the spectrum for the clean crystal at 500K, Panel (b) is the spectrum for the 500K crystal with 0.048ML of oxygen. It is clear that the new mode  $E_1$  disappears upon oxygen dosing. Right side is out-of-phase data: panel (c) is the spectrum for the clean crystal at 250K, Panel (d) is the spectrum for the 250K crystal with 0.048ML of oxygen. The new mode  $E_2$  disappears upon oxygen dosing.

**Figure 19.** Panel (a) shows our analytic model fit to the  $E_1$  mode. Panel (b) shows the three phonon modes of the 1D lattice confined in the 2D anisotropic harmonic potential plotted together with the experimental results. See Ref. 15 for further details.

**Figure 20.** Time-resolved helium diffraction data for a superlattice (ordered alloy) peak of  $Cu_3Au(001)$  following quenches from 720 K to 650 K, which is about 5.5 degrees below the bulk ordering temperature of the alloy. These data reveal a surface ordering time on the order of a minute, whereas the bulk requires about an hour to order under similar quench conditions. Three panels are for reproduced data sets taken sequentially.

**Figure 21.** Evidence for the abrupt onset of multphonon scattering from  $Cu_3Au(001)$  about 20 degrees below the bulk disordering temperature of the alloy. Between 642 K and 647 K the multiphonon (broad background) contribution increases substantially on the annihilation side of the spectra. The spectra then retain a similar appearance from 647 K up through  $T_c$  (665 K) for the bulk. This observations emphasizes the role that anharmonicity plays in the elevated temperature dynamics of this alloy.

**Figure 22.** The dispersion of the dipole active NO internal stretch along the two high symmetry directions of the Ni(111) substrate for the 0.5ML c(4x2) overlayer (a), and the 0.4ML overlayer (b). The solid lines are the fits to the data using the dipole-dipole coupling model as explained in the text.

**Figure 23.** Schematic diagram of the very efficient plasma beam source we propose to use for the production of intense supersonic beams of atomic oxygen, including  $O(^3P)$  and  $O(^1D)$  species, as well as other energetic reagents such as  $O_2(^1\Delta)$  and atomic hydrogen.

**Figure 24.** Schematic view of the new UHV-STM facility. Samples and spare scanners can be inserted via a load-lock (not shown). The chamber's frame rests on four "laser-table" air shocks for enhanced vibrational damping of the system. The Omicron micro-STM (already in hand) is currently being modified for elevated-temperature operation. This very compact STM head has an integrated walker capability which allows us to survey widely spaced areas of the sample. Provisions have been included in the chamber's design to accomodate future top-loading and cryogenically cooled STM heads for low-temperature imaging experiments.

FIGURE 1

34

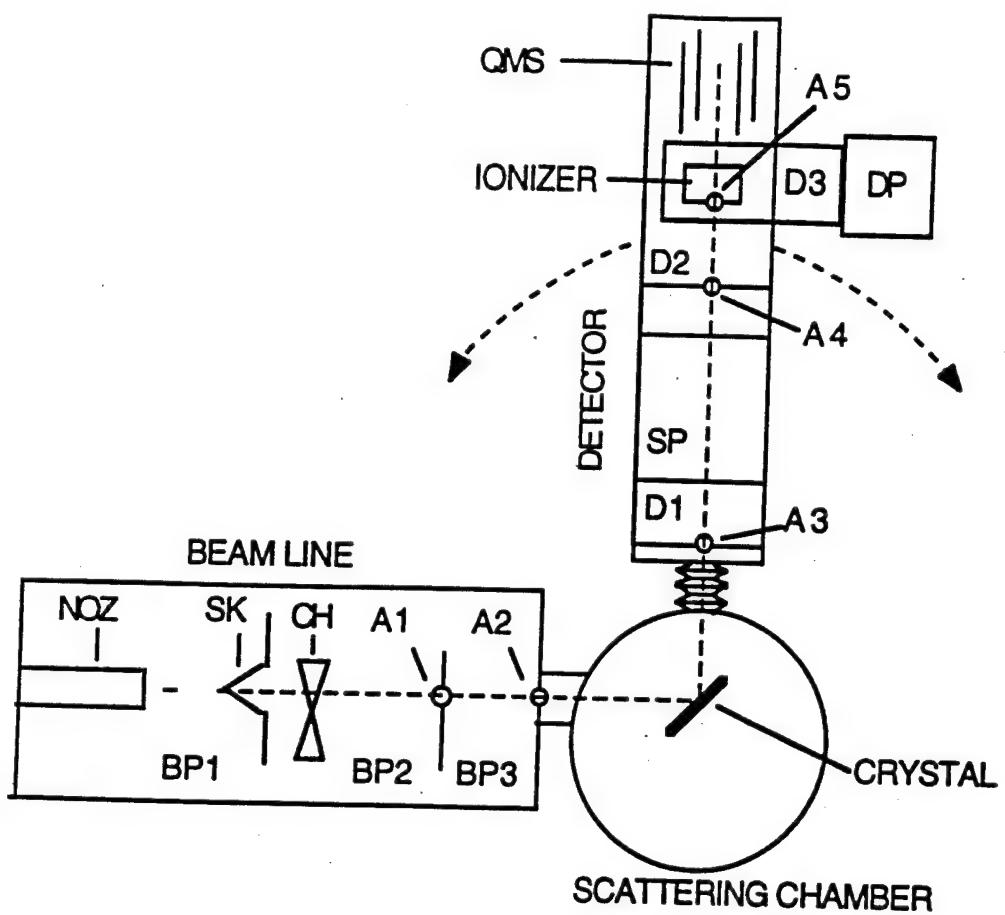


FIGURE 2

35

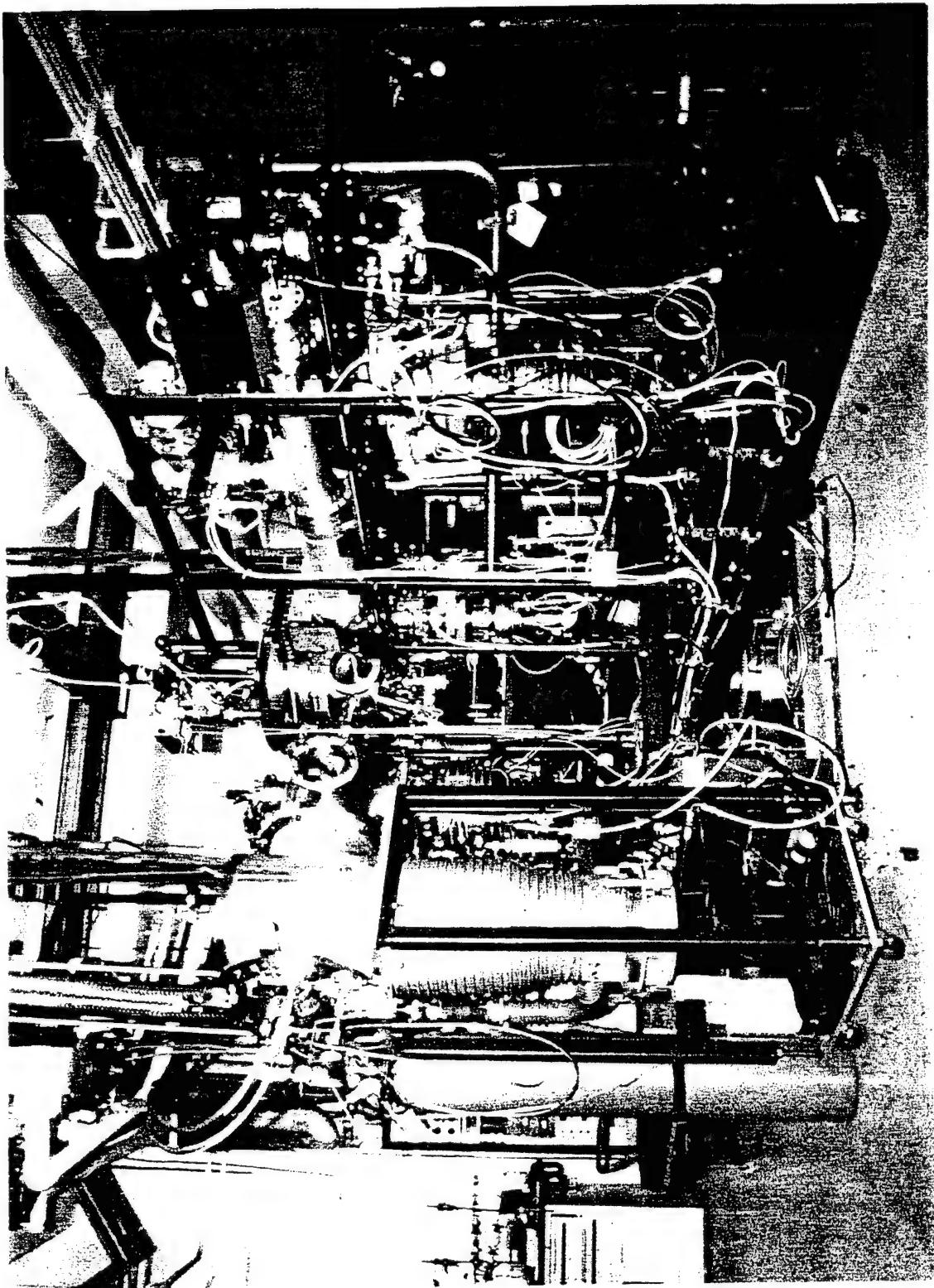


FIGURE 3

36

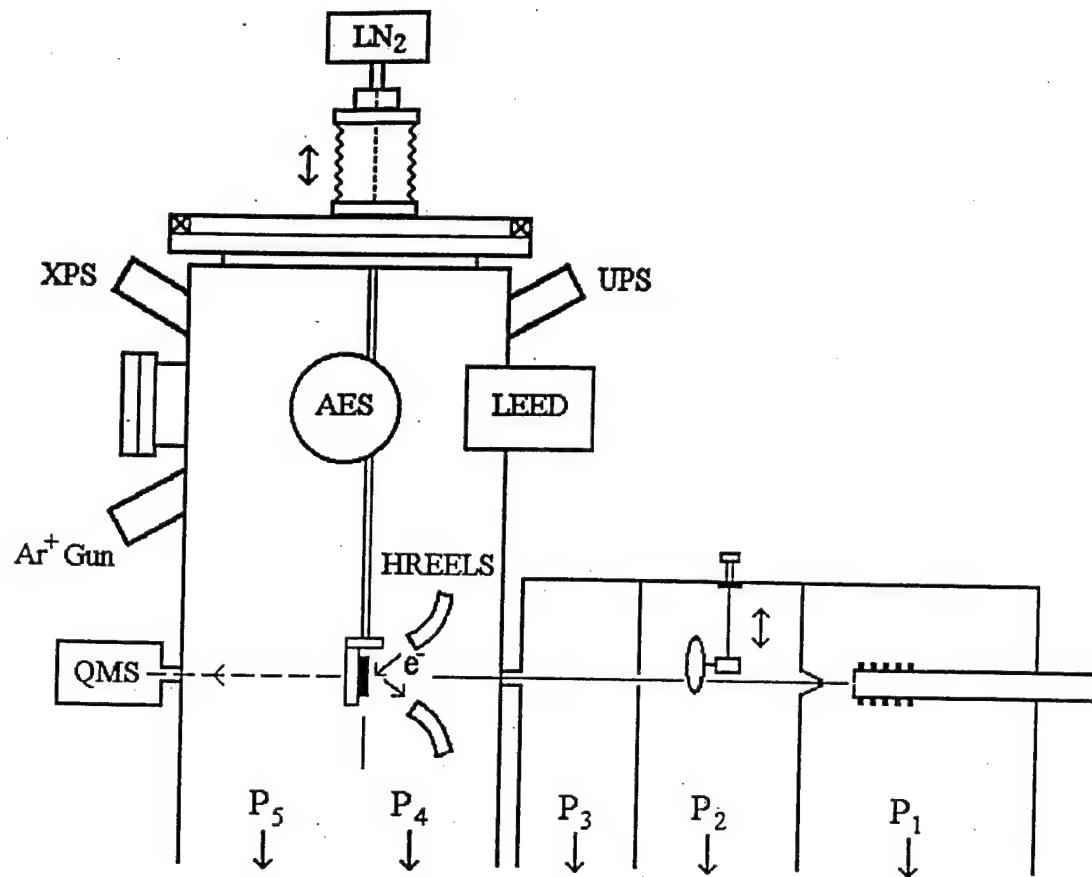


FIGURE 4

37

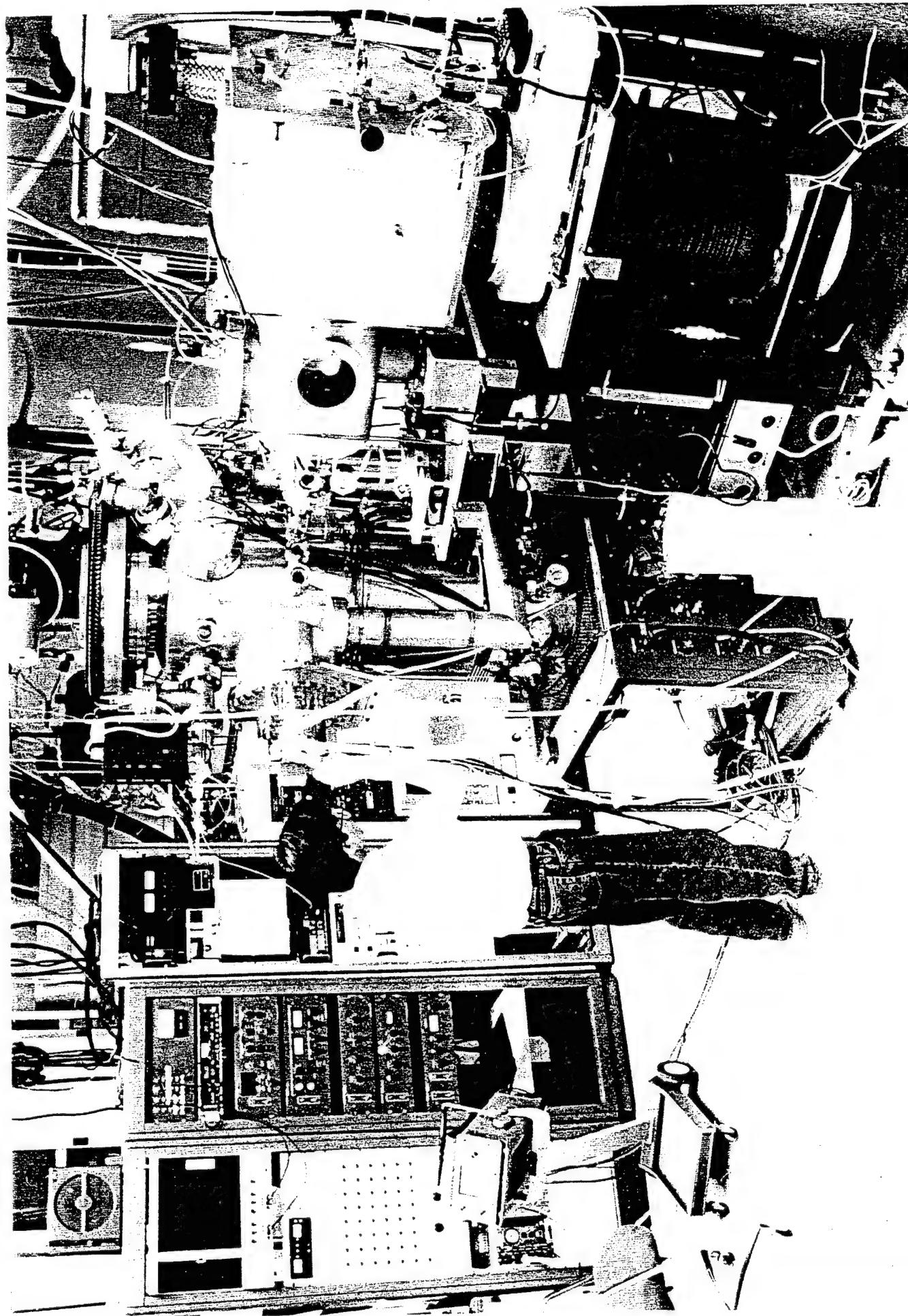


FIGURE 5

38

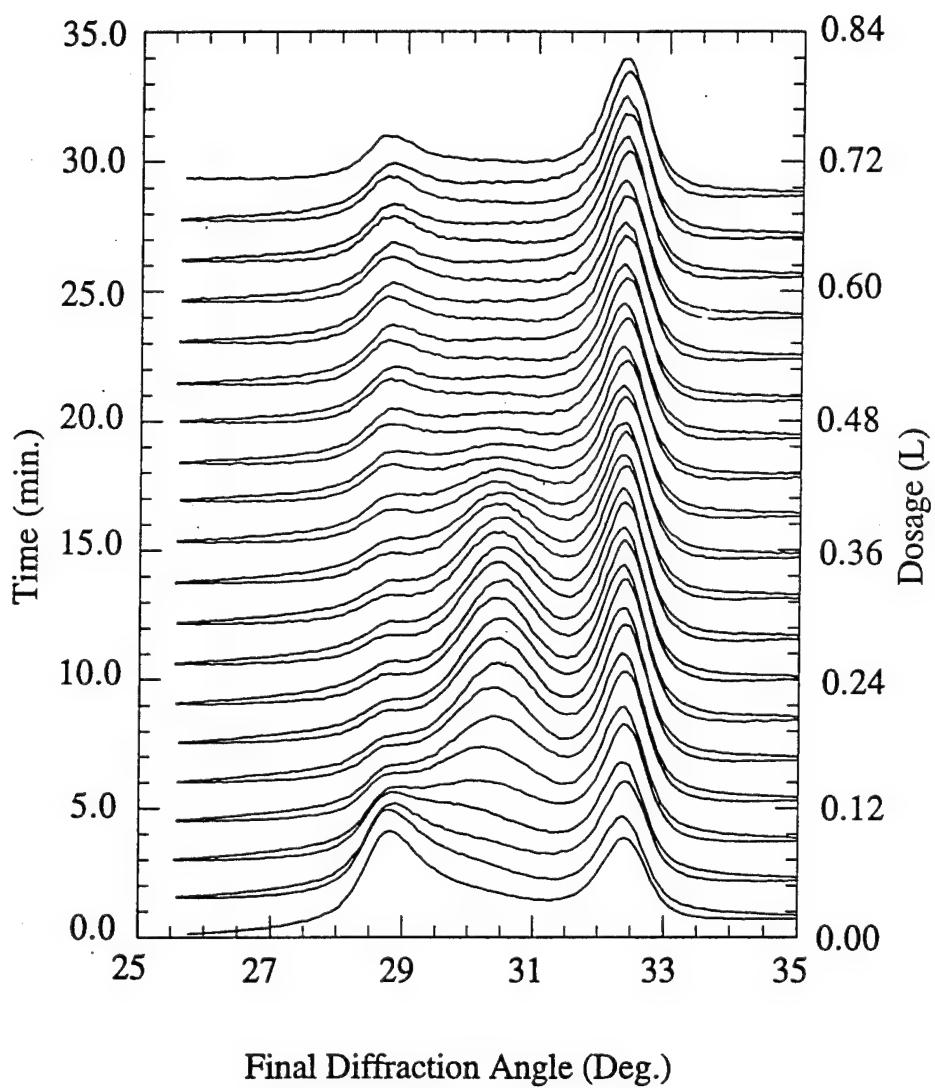


FIGURE 6

39

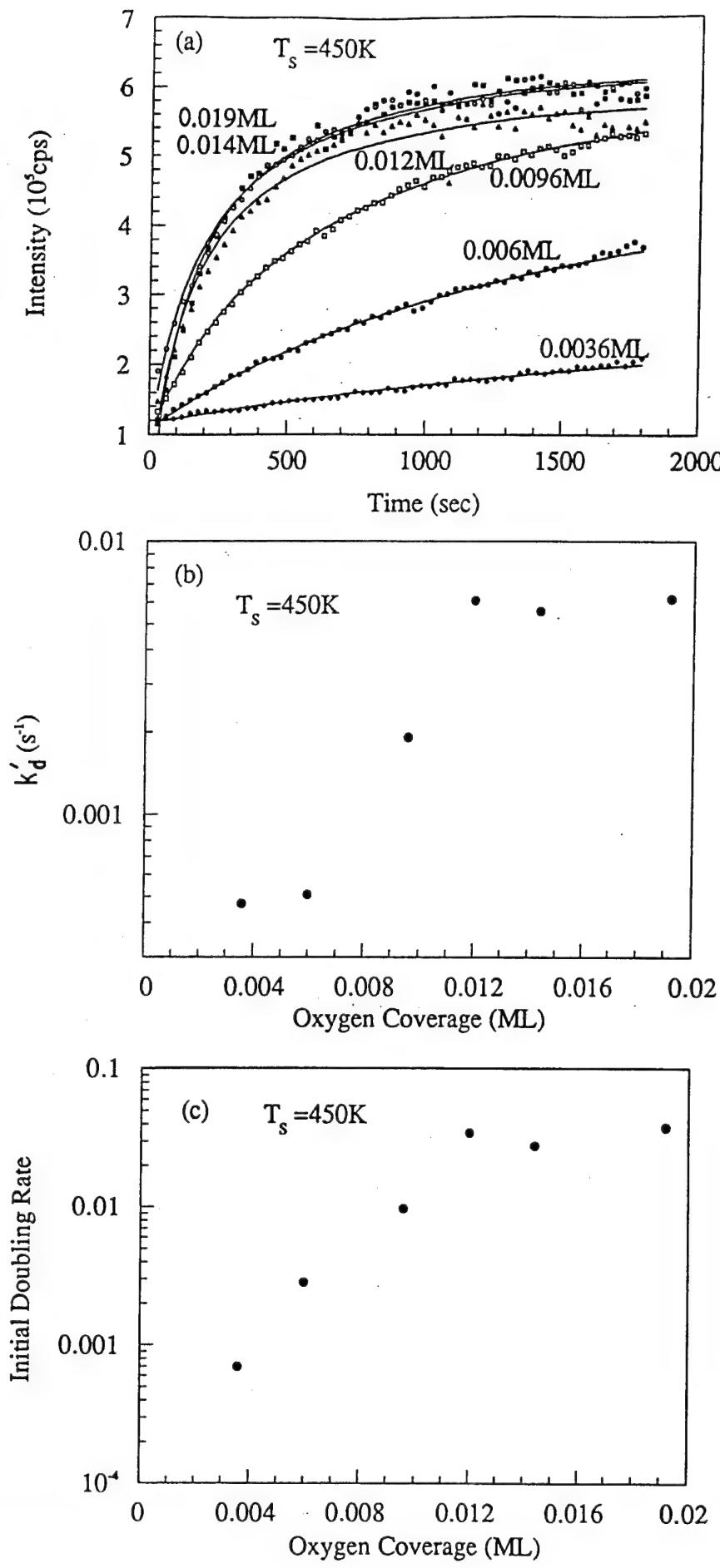


FIGURE 7

40

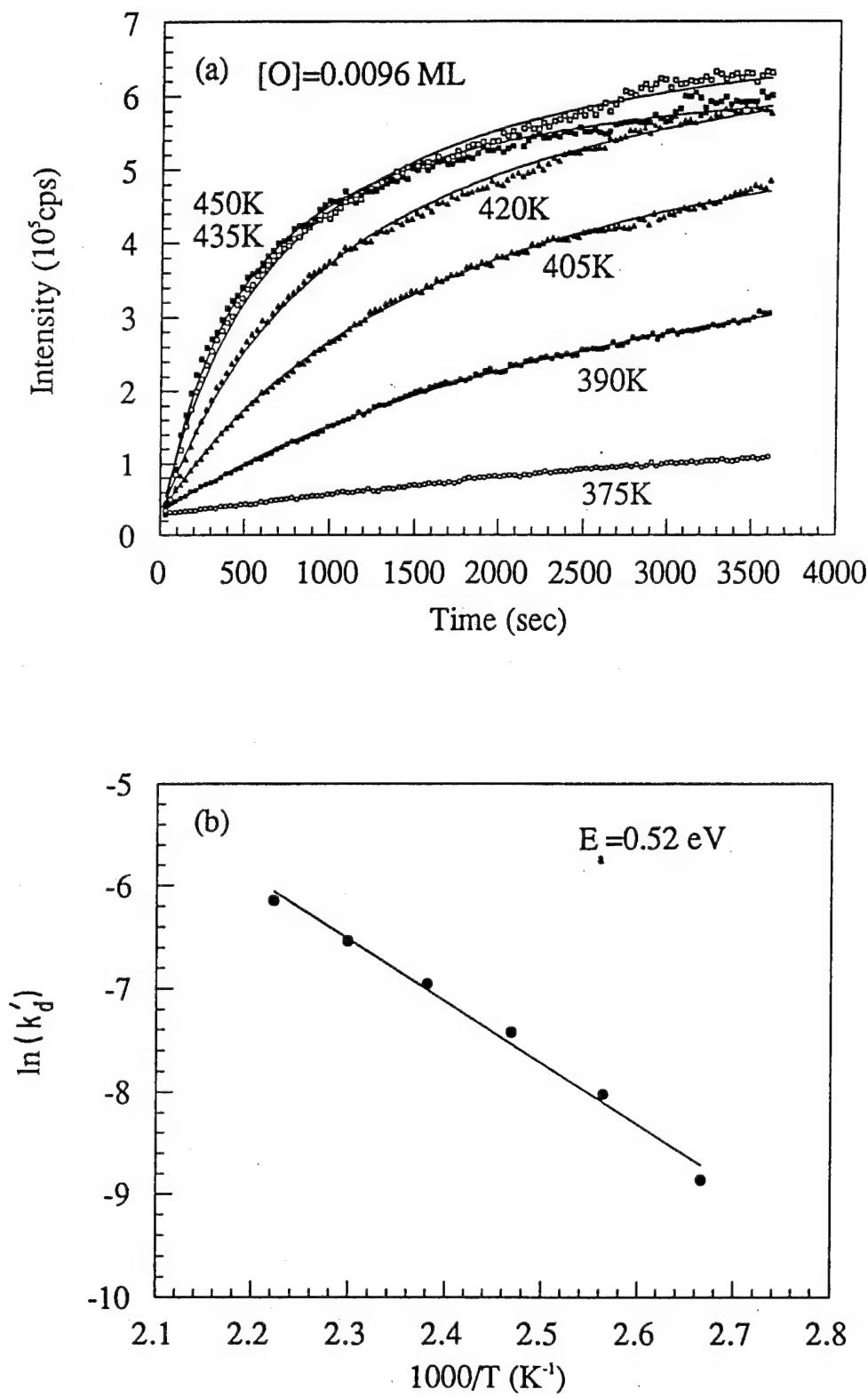


FIGURE 8

41

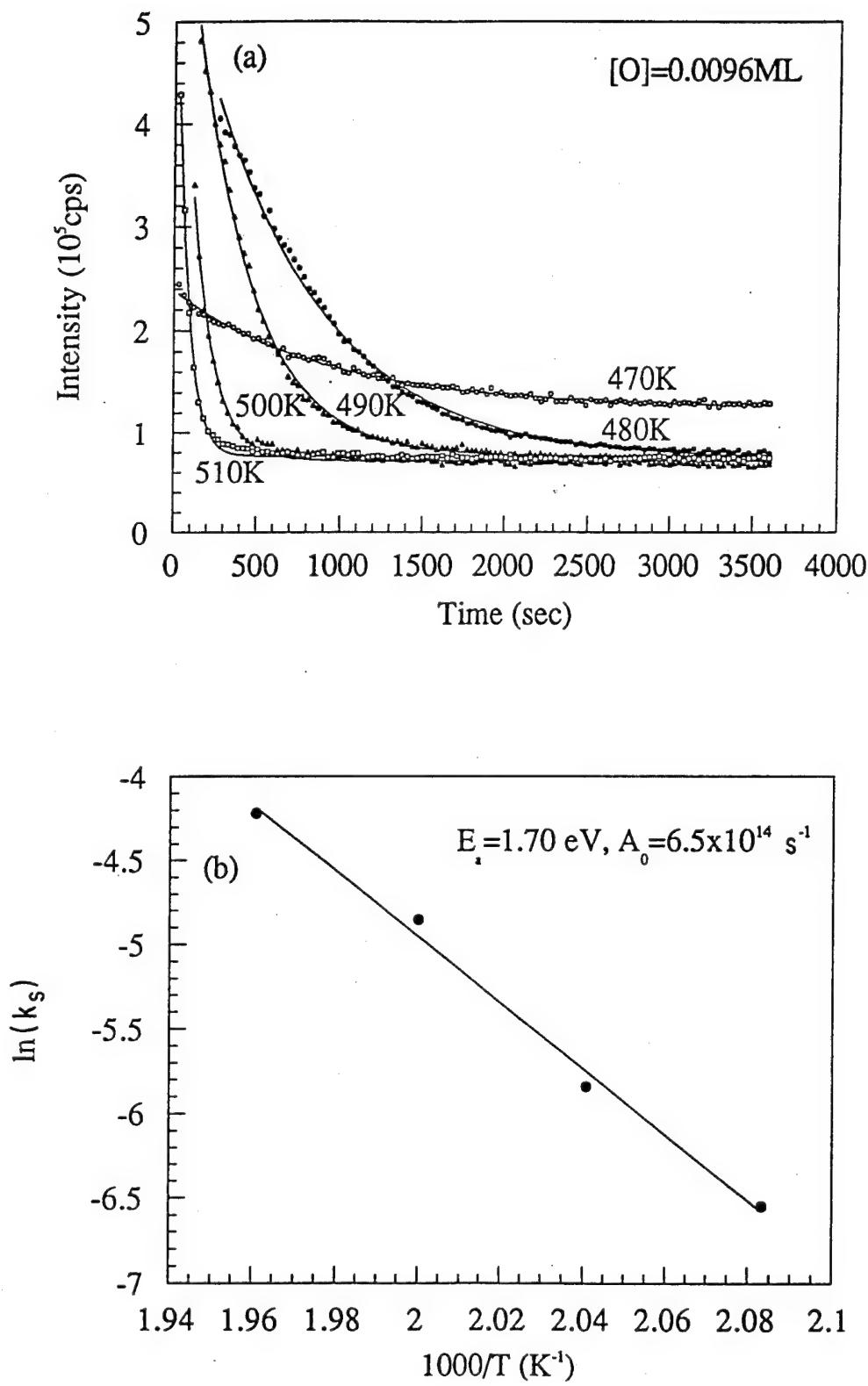


FIGURE 9

42

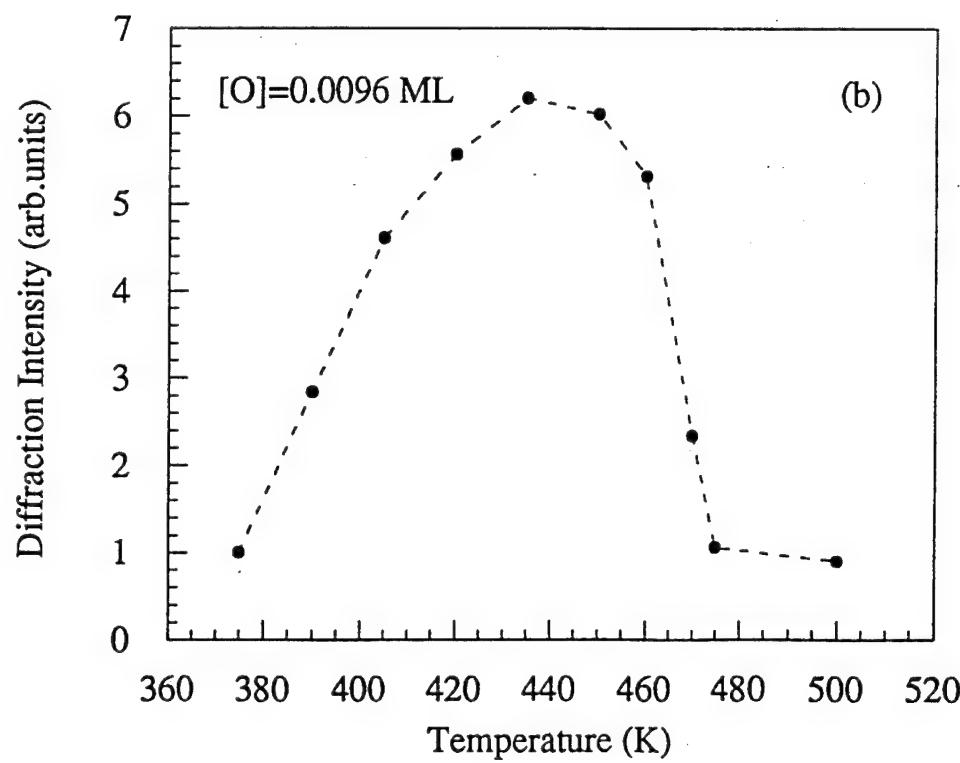
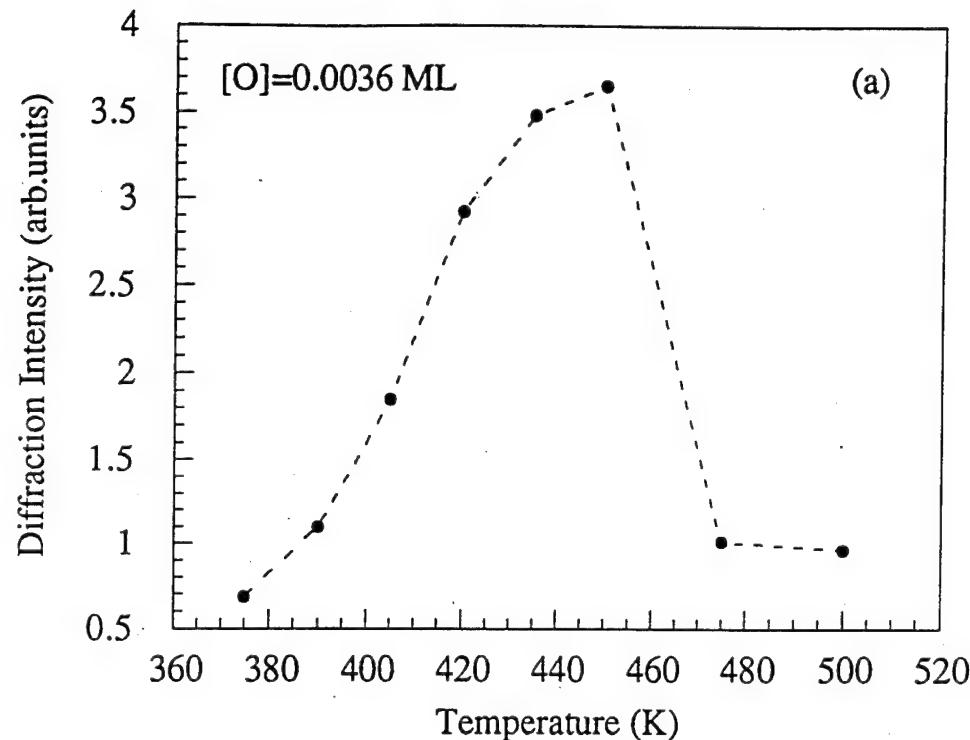


FIGURE 10

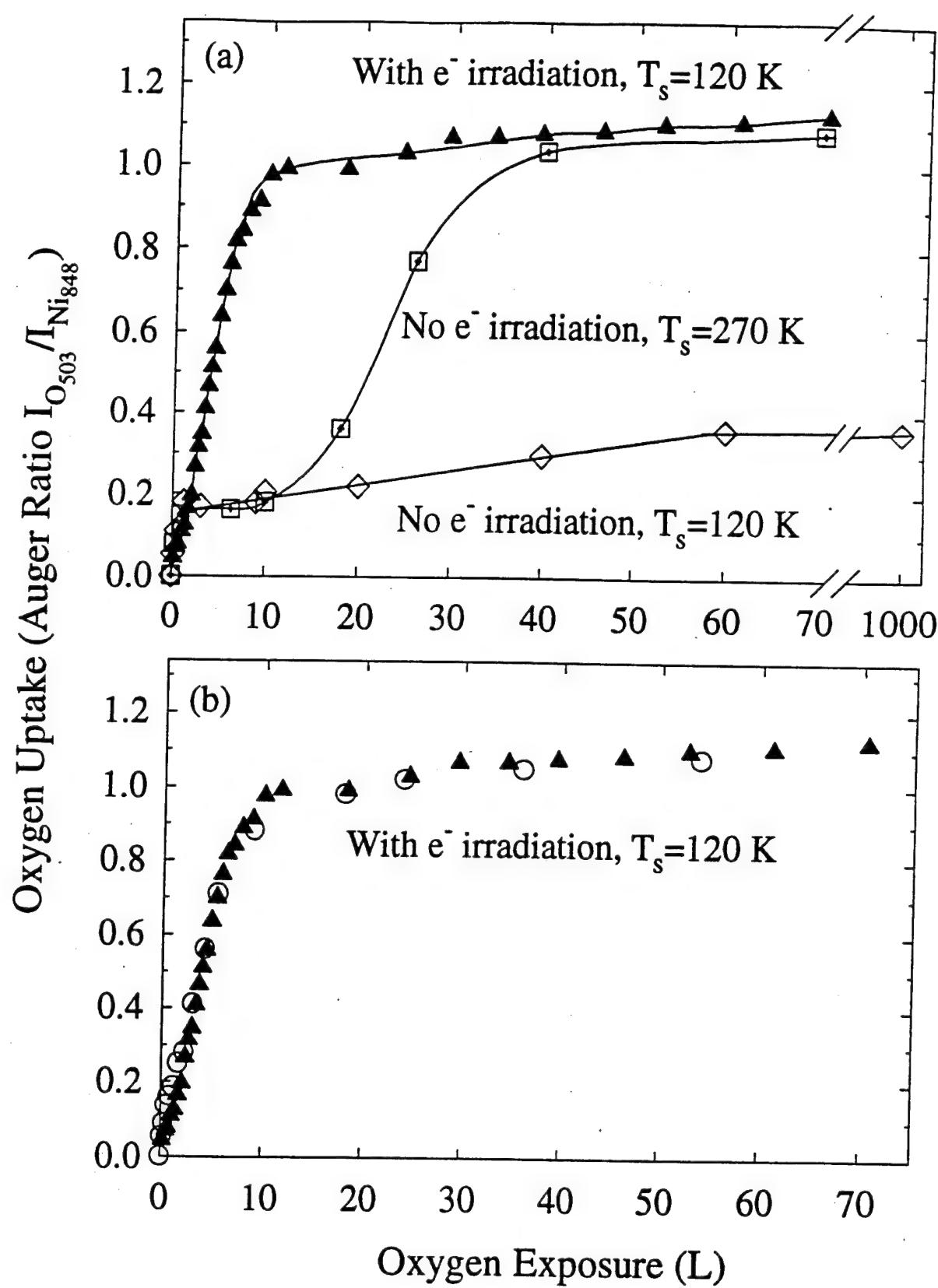


FIGURE 11

44

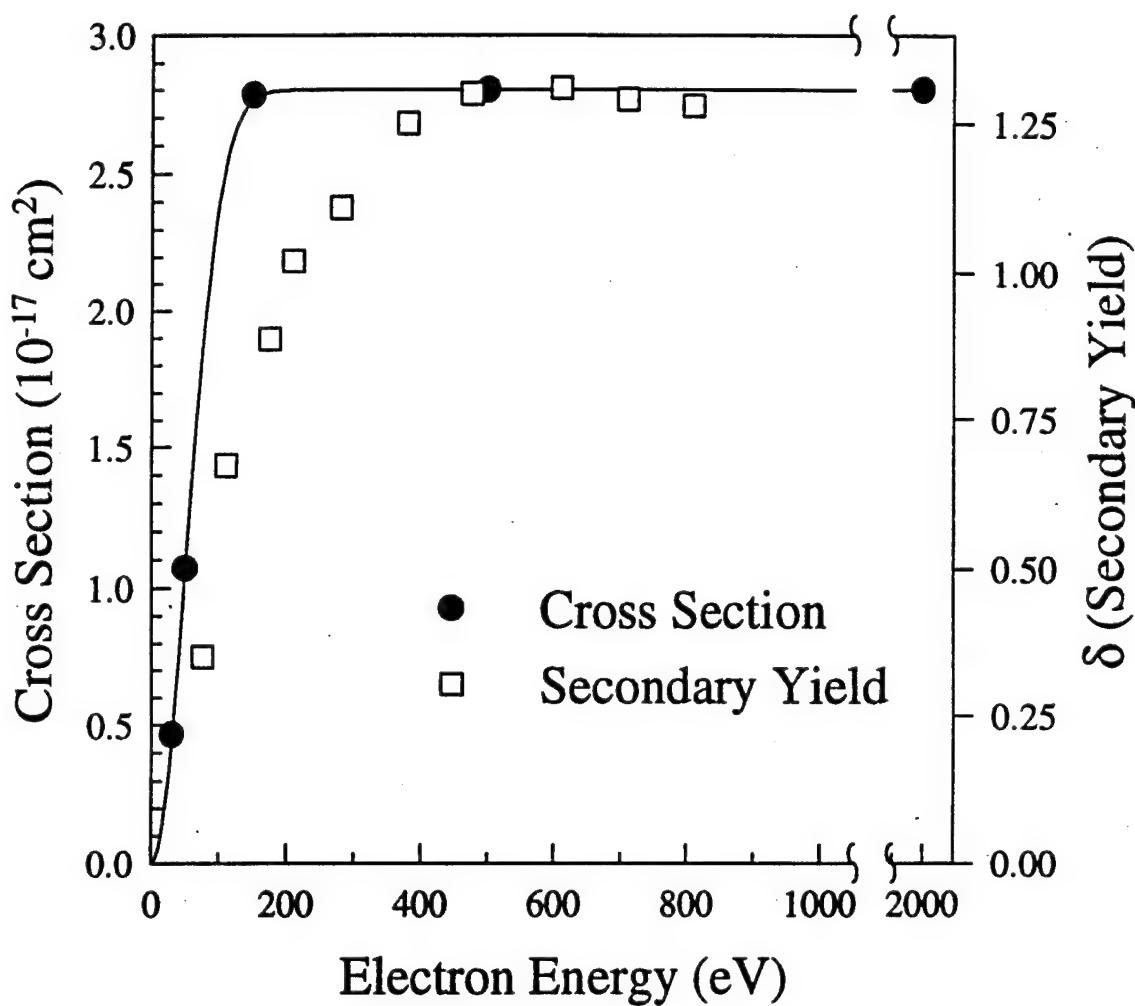


FIGURE 12

45

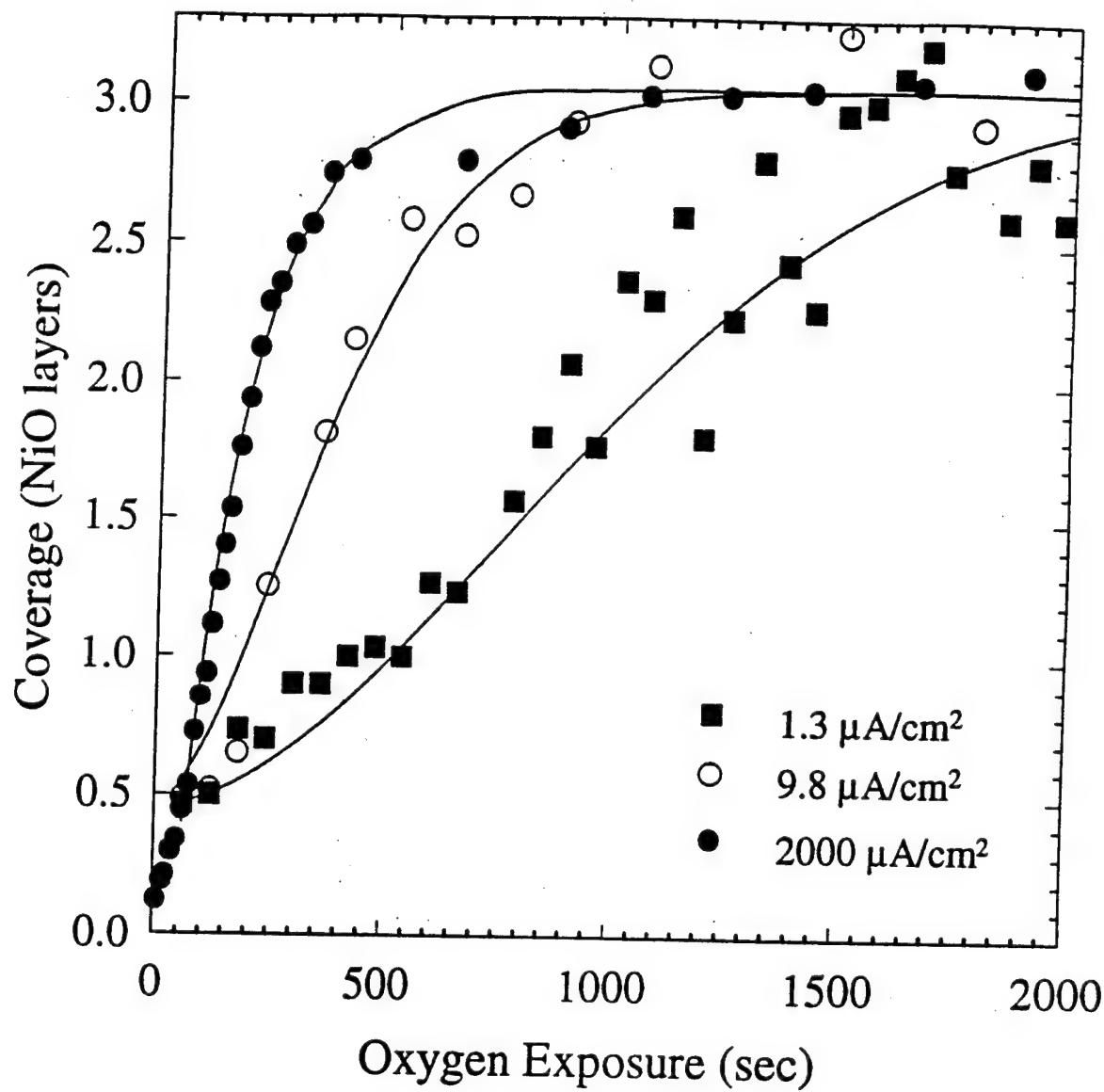


FIGURE 13

46

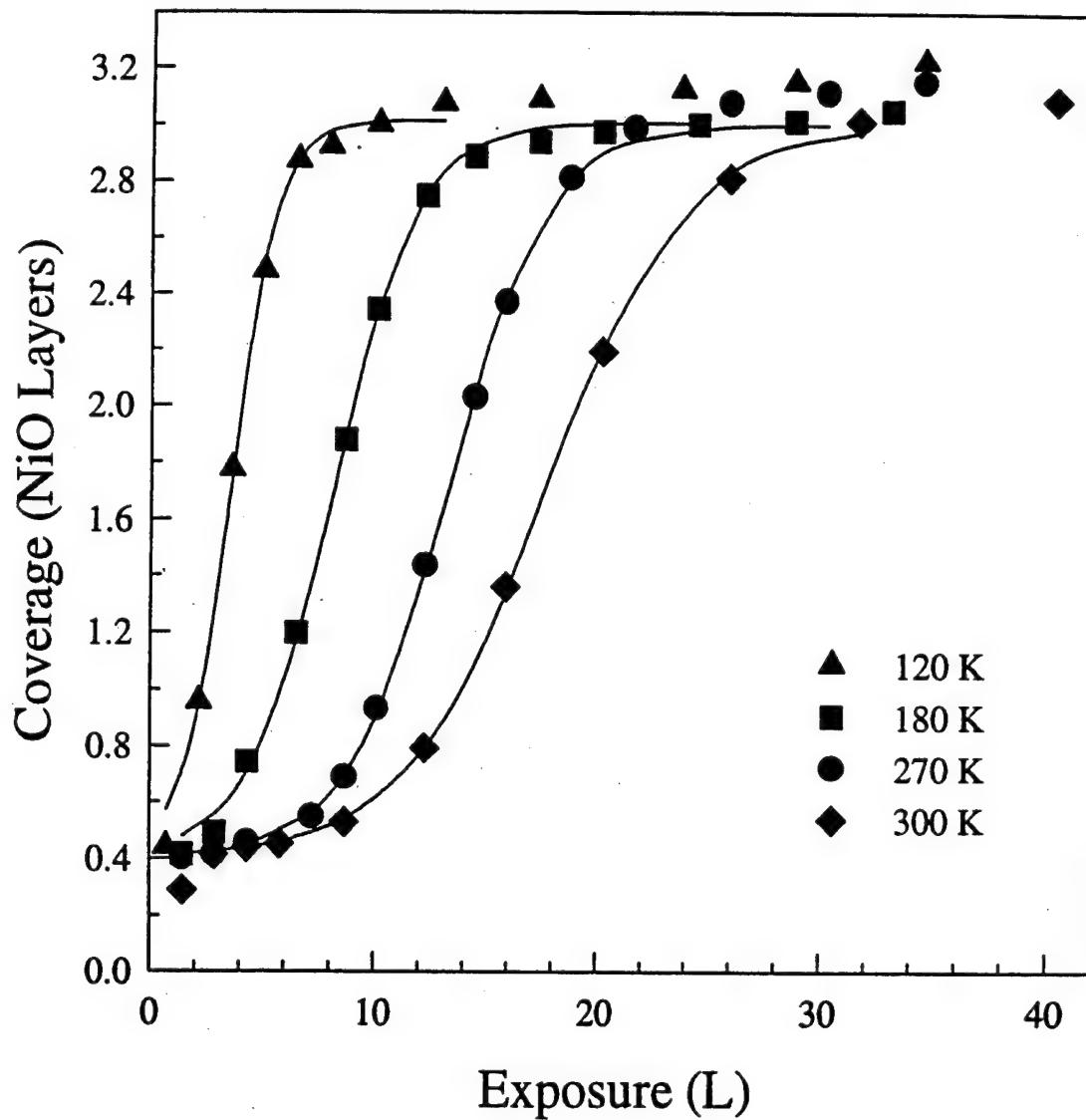


FIGURE 14

47

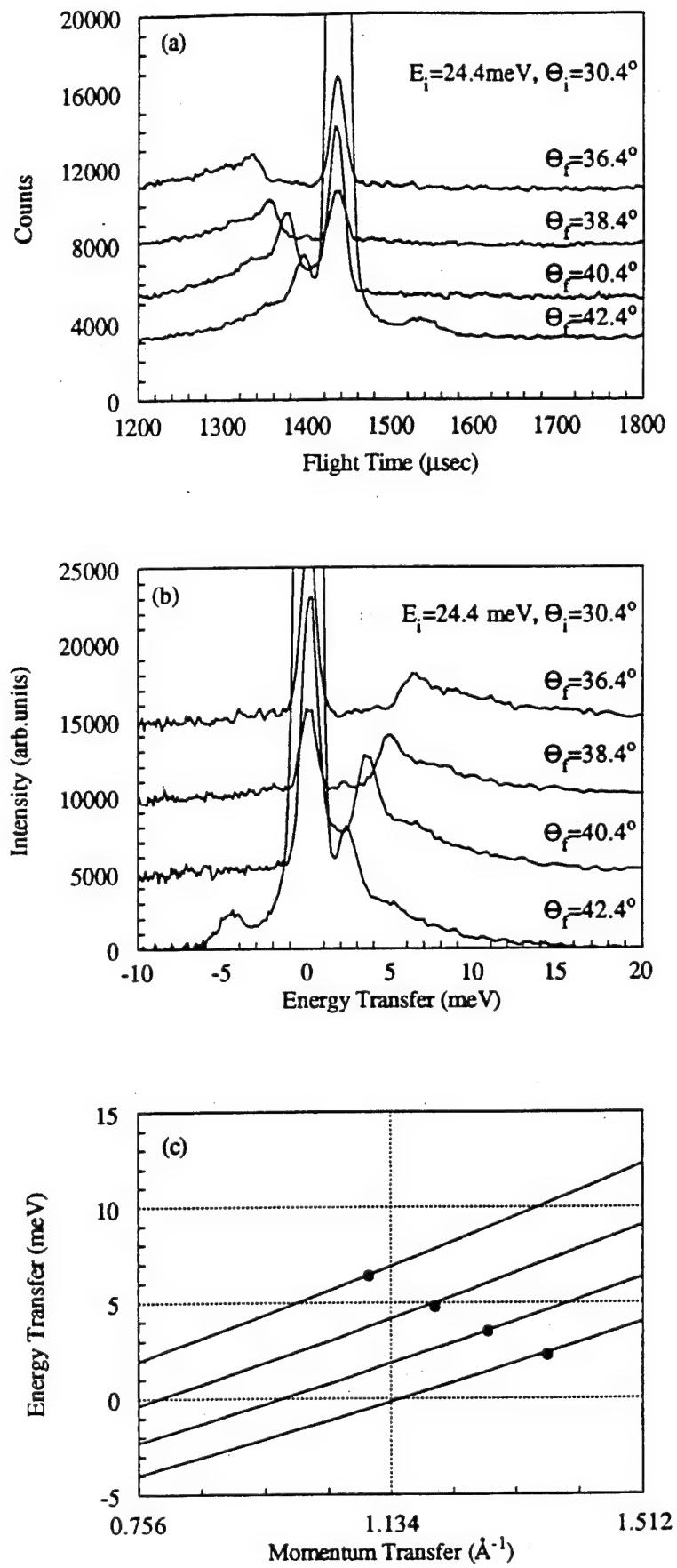


FIGURE 15

48

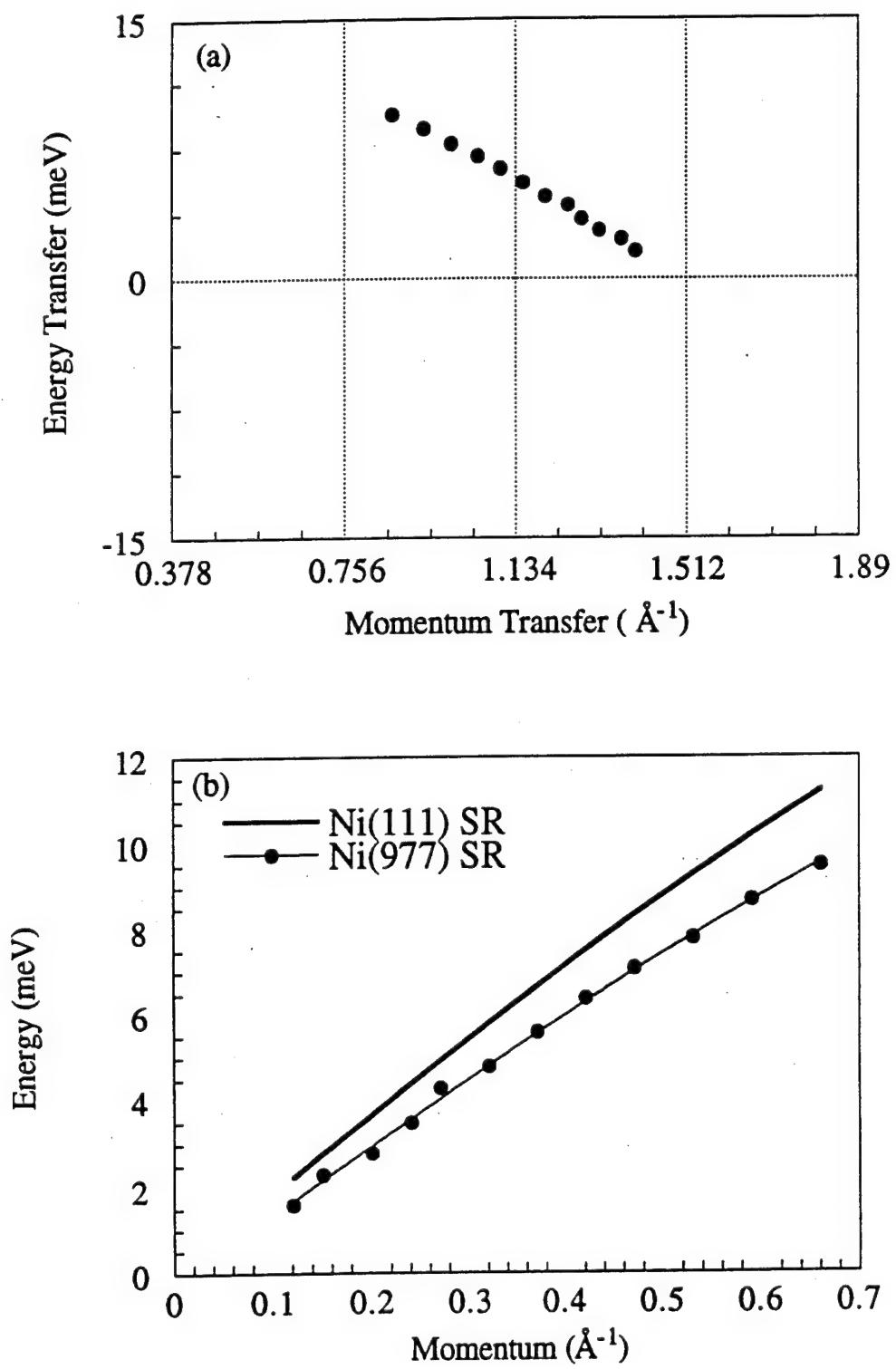


FIGURE 16

49

Ni(977)

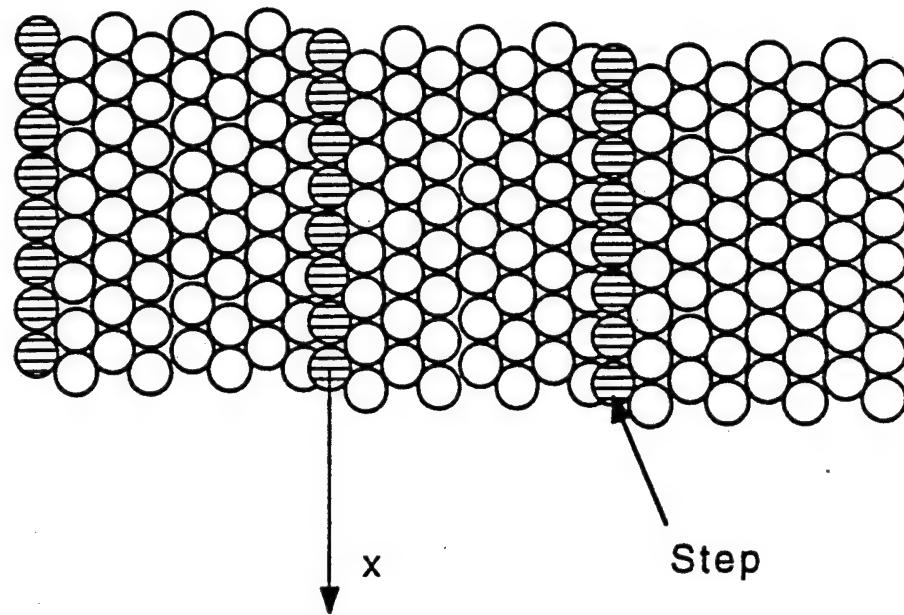


FIGURE 17

50

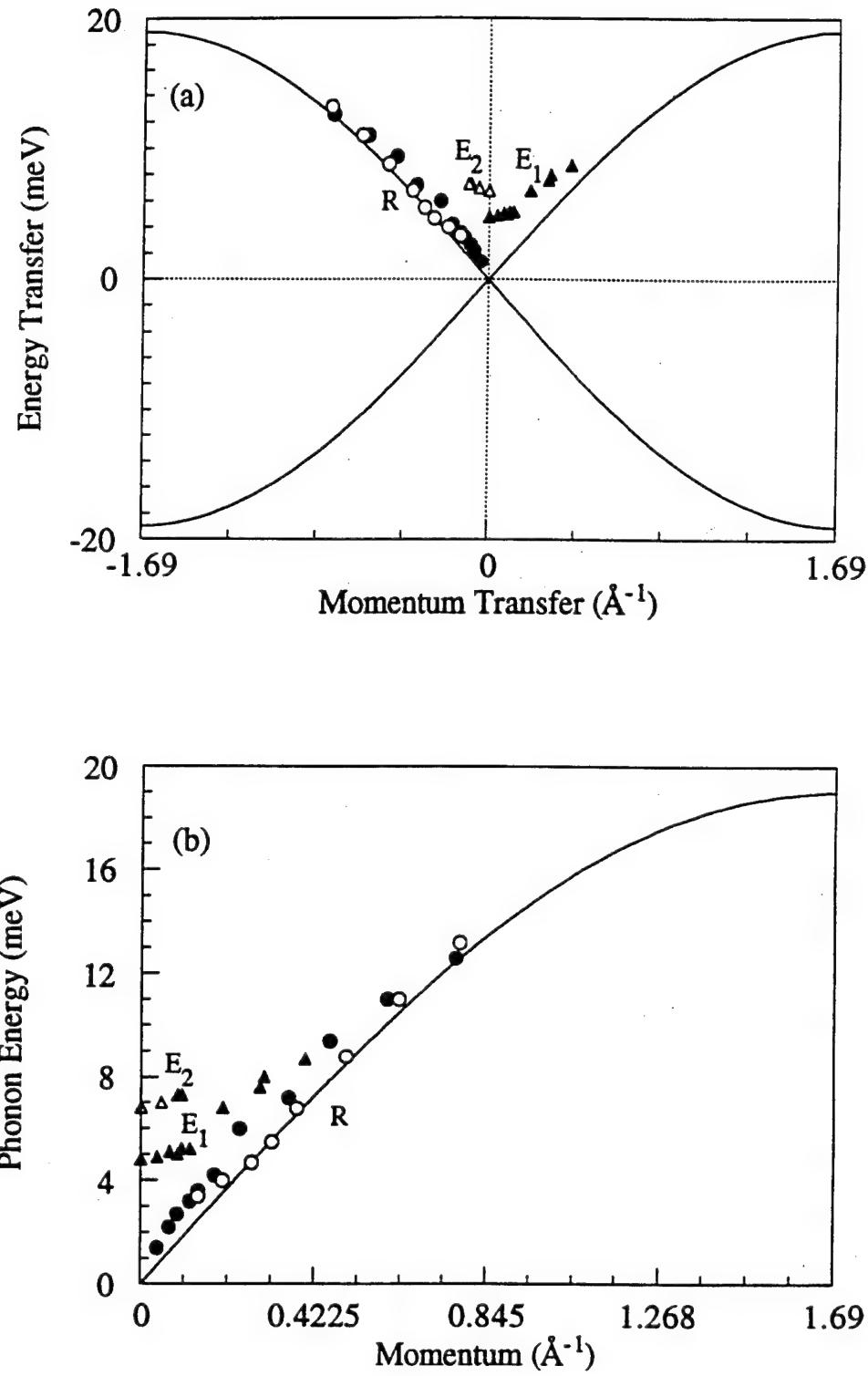


FIGURE 18

51

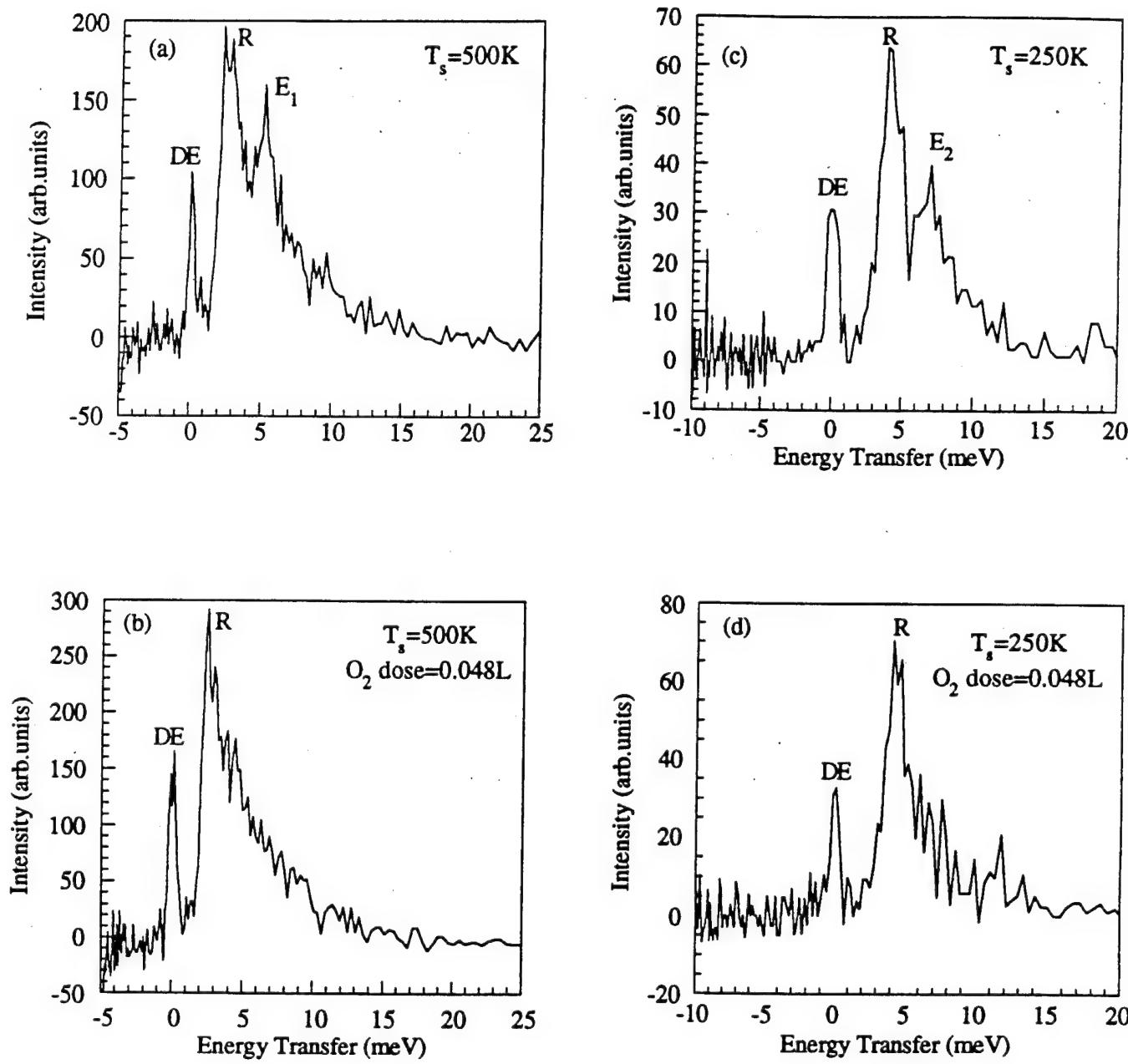


FIGURE 19

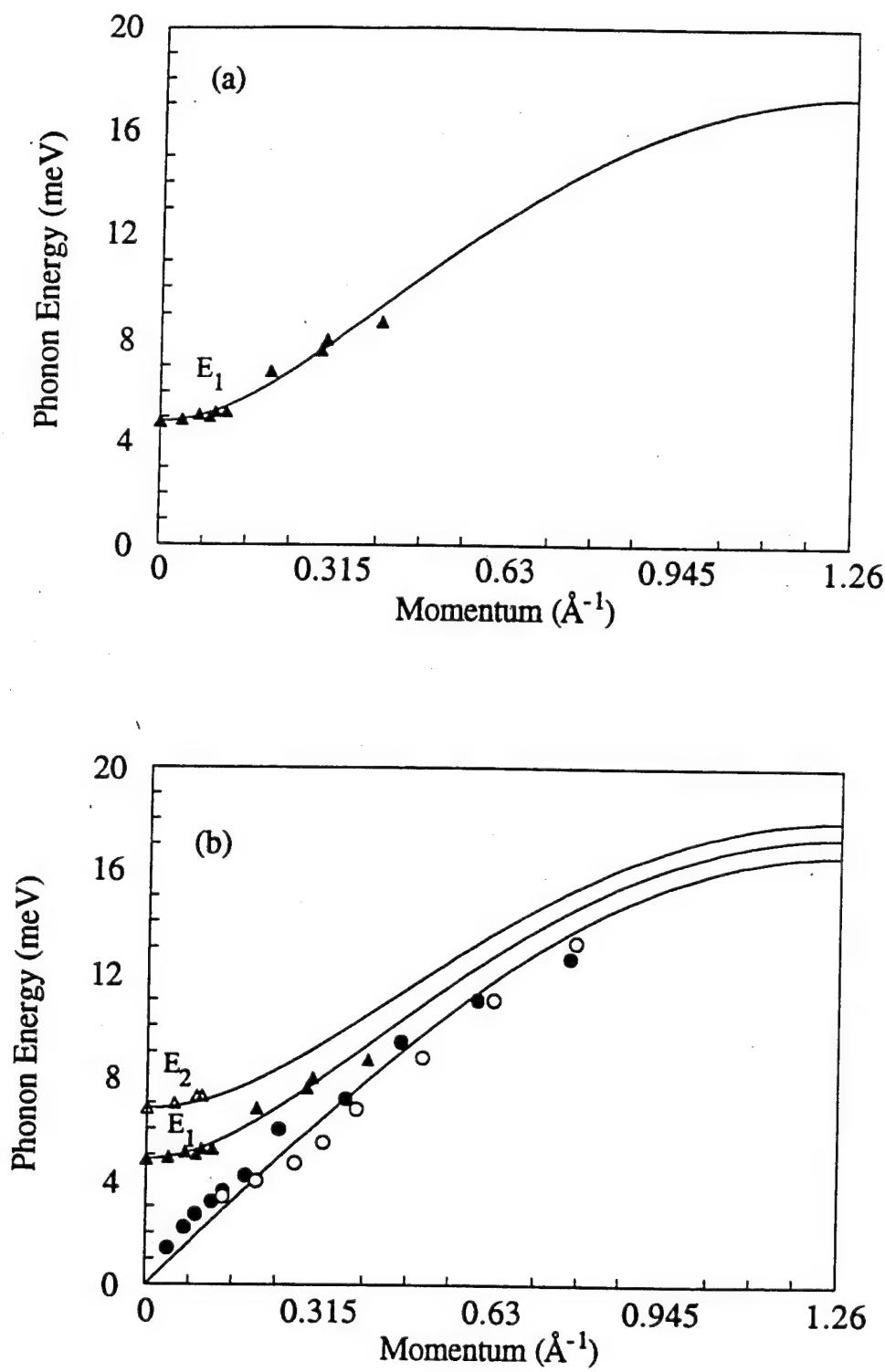


FIGURE 20

53

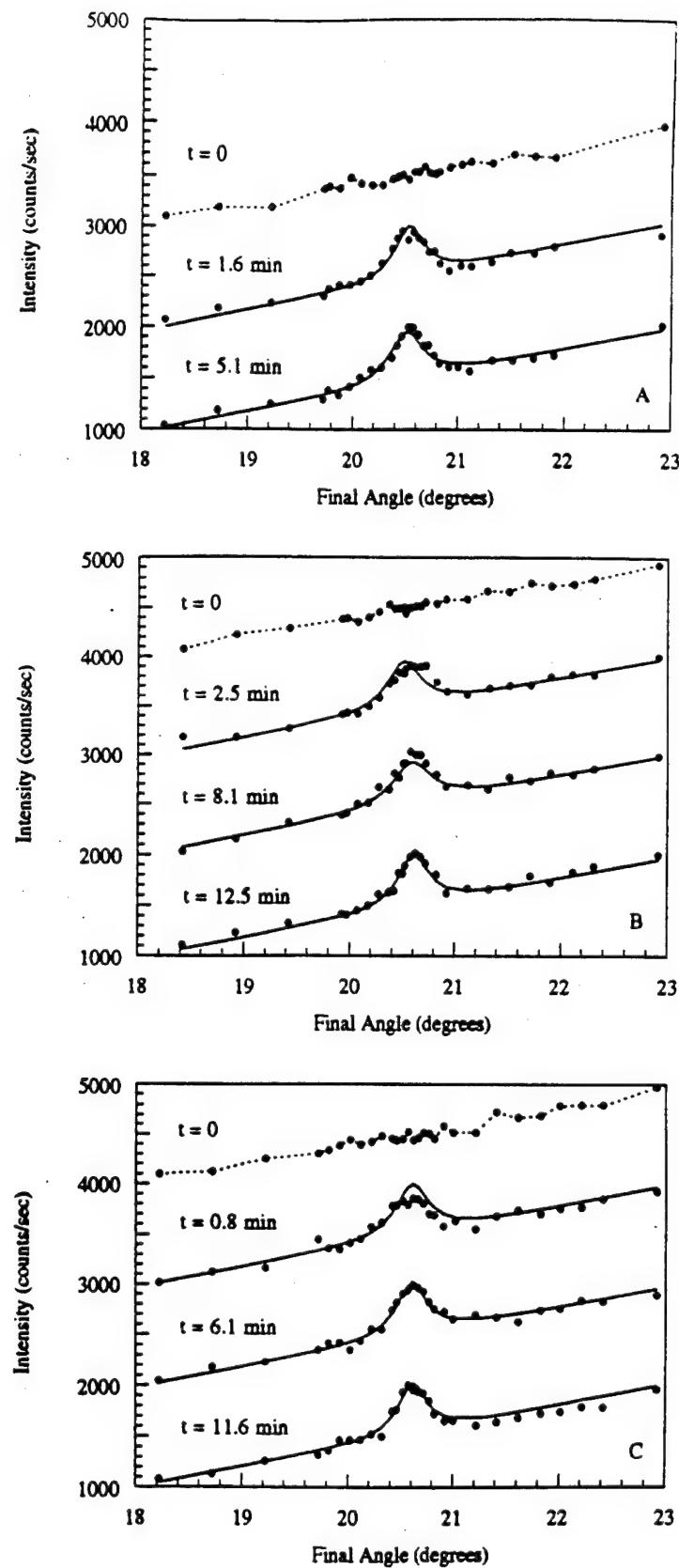


FIGURE 21

54

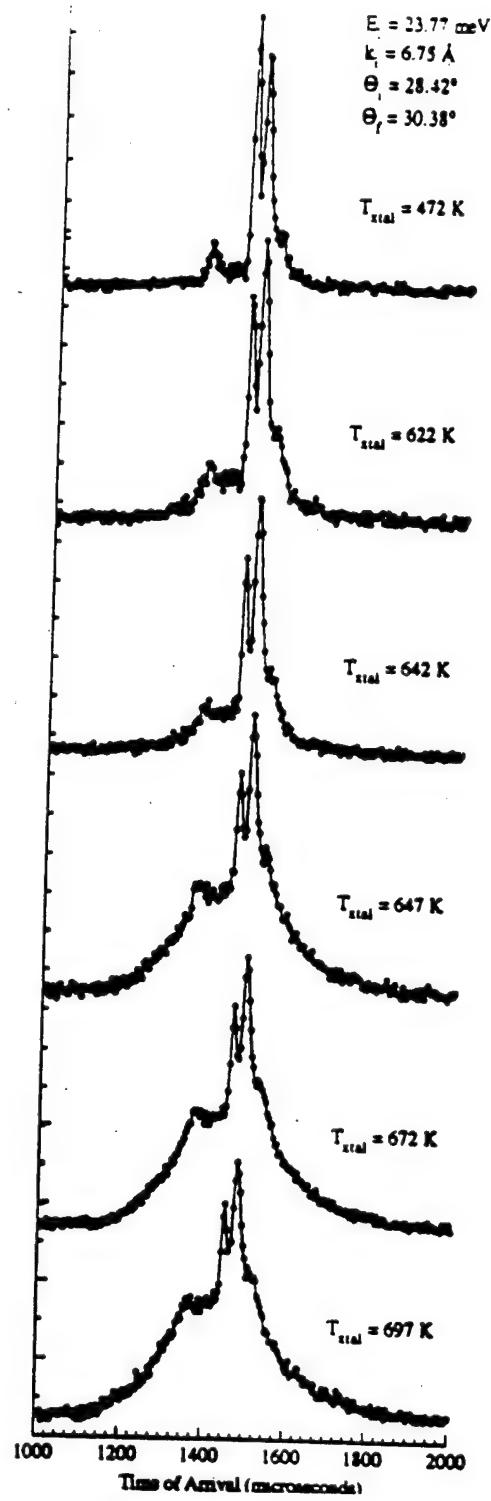


FIGURE 22

55

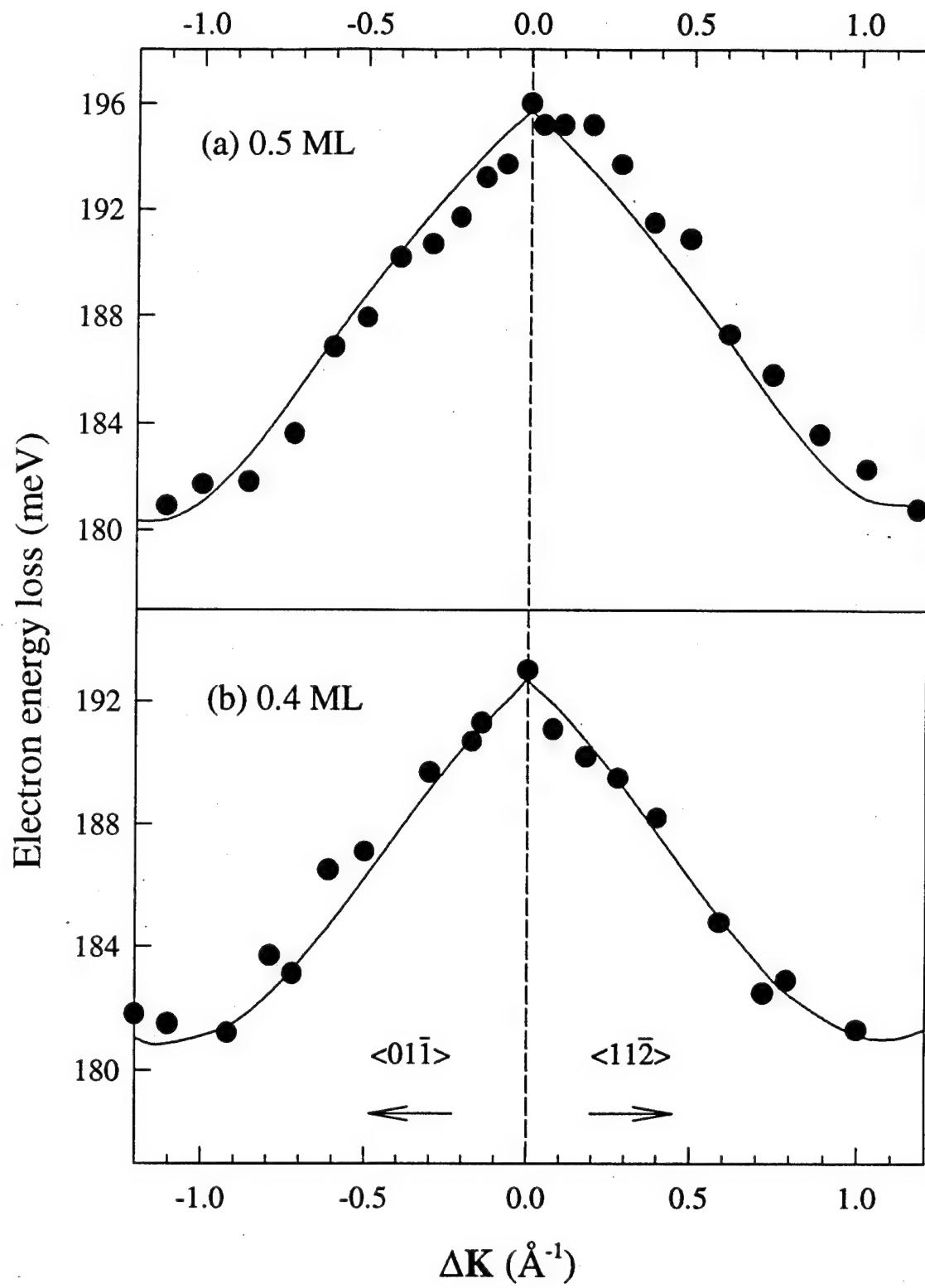
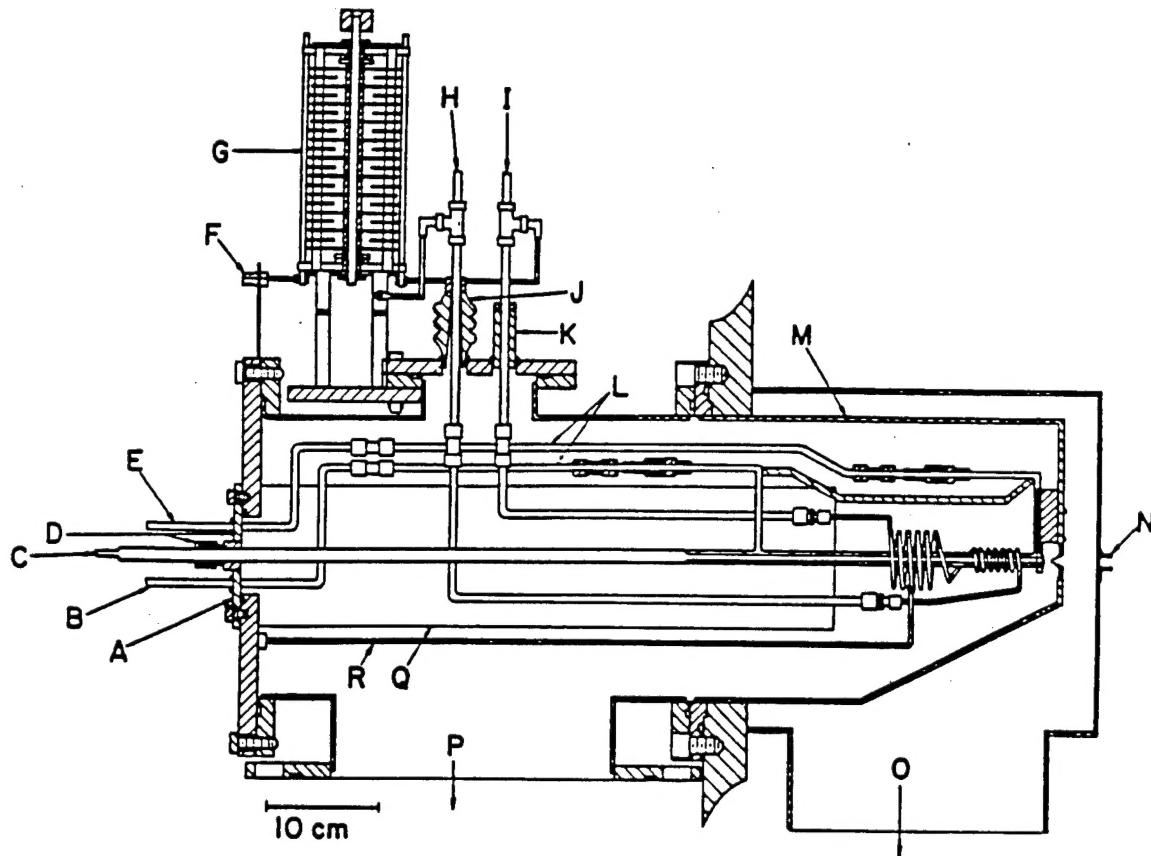


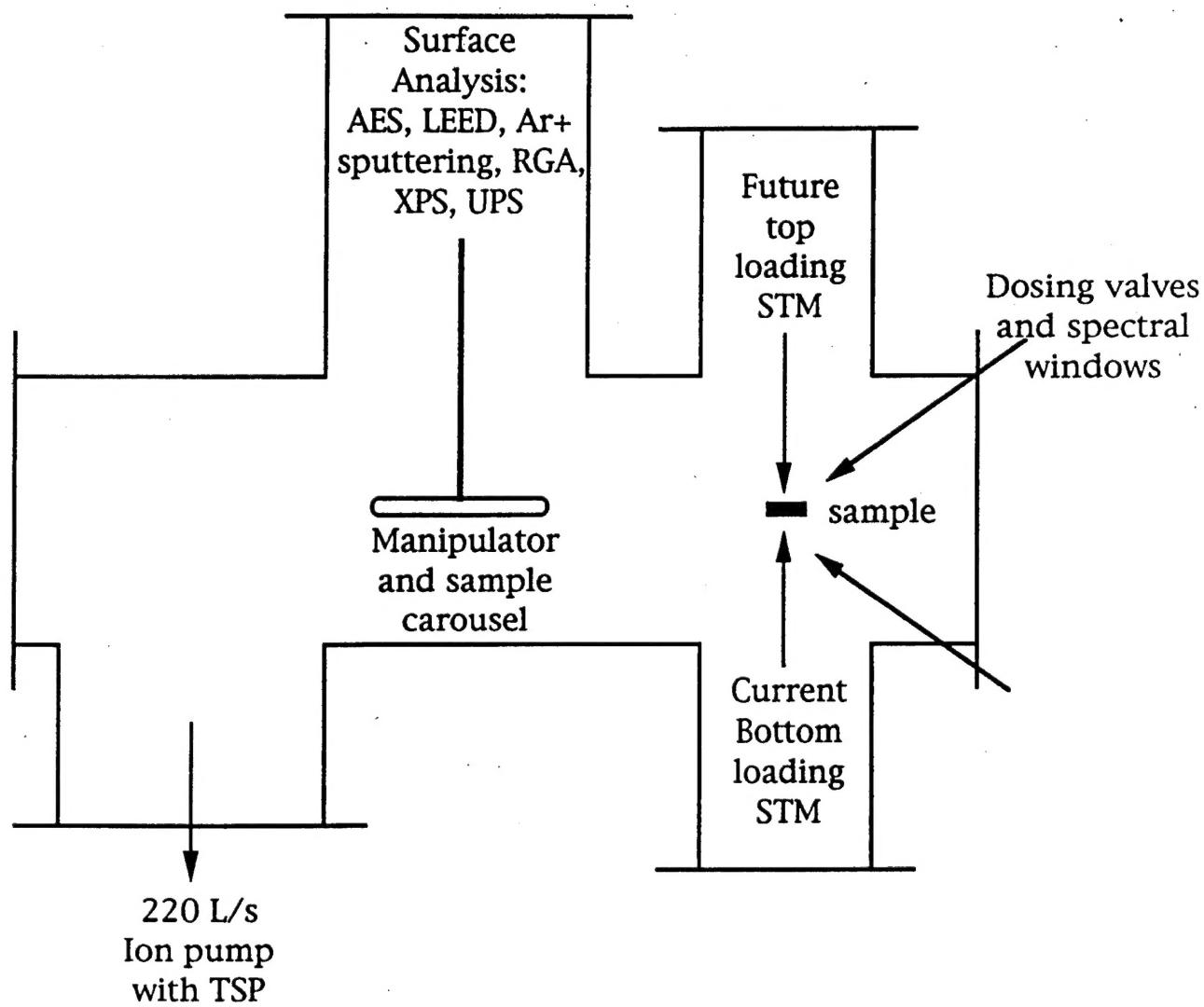
FIGURE 23



Sectioned view of the plasma beam source mounted in a differentially pumped chamber. A-Lucite insulating flange. B-Nozzle coolant return. C-Quartz nozzle gas inlet. D-Cajon ultra-torr fittings. E-Nozzle coolant inlet. F-RF power input from RG-213/u coaxial cable. G-Variable air capacitor. H-Coupling coil coolant outlet. I-Coupling coil coolant inlet. J-Ceramic feedthrough for RF return and coil coolant. K-Ceramic feedthrough for RF input and coil coolant. L-Poly-Flo tubing sections. M-Stainless steel source chamber. N-Plates for 5000 V/cm ion deflecting field. O-1200 l/sec diffusion pump, differential region. P-4200 l/sec diffusion pump, source region. Q-Epoxy resin Mechanical support. R-Electrical ground wire. Not shown: Wire mesh RF shielding which covers the air capacitor/RF feedthrough assembly.

FIGURE 24

UHV-STM Chamber Schematic-Side View



## VI. Curriculum Vitae - Steven J. Sibener

<u>Born</u>	April 3, 1954; Brooklyn, New York
<u>Education</u>	1971-1975 University of Rochester, Rochester, New York. Sc.B. in Chemistry awarded with High Distinction, 1975. B.A. in Physics awarded with Distinction, 1975.
	1975-1979 University of California, Berkeley. M.S. in Chemistry, 1977. Ph.D. in Chemistry, 1979. Research with Professor Yuan T. Lee.
<u>Professional Experience</u>	Eastman Kodak Research Laboratories, Photographic Research Division, Summer 1974: Electrostatic properties of polymers and polymer-metal interfaces.  Eastman Kodak Research Laboratories, Physics Division, Solid StatePhysics Research Laboratory, Summer 1975: Oxide growth on GaAsP for MOS fabrication.  Bell Laboratories Postdoctoral Fellow, September 1979 - August 1980. Research with Dr. M.J. Cardillo involving molecular beam scattering from single crystal surfaces.  The University of Chicago, The James Franck Institute and The Department of Chemistry: Assistant Professor, August 1980 - June 1985. Associate Professor, July 1985 - June 1989. Professor of Chemistry, July 1989 - .
<u>Honors and Awards</u>	Chairman, Div. of Chemical Physics, American Physical Society, 1996. Visiting Fellow, Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, 1992-93. Marlow Medal of the Faraday Division of the Royal Society of Chemistry, 1988. IBM Faculty Development Award, 1984-86. Alfred P. Sloan Foundation Research Fellow, 1983-87. Camille and Henry Dreyfus Young Faculty in Chemistry Award, 1980. Gulf Oil Research Fellow, University of California, Berkeley. American Institute of Chemists Award, University of Rochester. American Chemical Soc. Div. of Colloid and Surface Chemistry Undergraduate Thesis Competition Honorable Mention: "The Shape of Liquid Interfaces," 1975. Regional Scholar for New York City, University of Rochester.
<u>Associations</u>	Phi Beta Kappa, American Physical Society, American Chemical Society, Royal Society of Chemistry, Sigma Xi, AAAS, American Vacuum Society

S.J. Sibener

**Curriculum Vitae (Continued)**

**Invited Lectureships**

Physikalisches Institut der Universität Erlangen-Nürnberg, 1988  
 Chemical Physics Institute Retreat Speaker, University of Oregon at  
 Eugene, 1992.  
 ACS Lecturer of the Analytical Chemistry Division, University of  
 Wisconsin, Madison, 1992.

**Consulting**

Dow Chemical USA (1982-1985)  
 Teltech Resource Network (1985- )  
 Institute for Defense Analyses (1985- )

**Professional Activities**

Vice-Chairman, 1985 Gordon Research Conference on the Dynamics  
 of Gas-Surface Interactions  
 Member, Defense Science Study Group--Institute for Defense  
 Analyses (1985 - 1988).  
 Member, Materials Research Laboratory Policy Committee, The  
 University of Chicago (1987 - ).  
 Chairman, 1987 Gordon Conference on the Dynamics of Gas-  
 Surface Interactions.  
 Member, International Advisory Committee of the Vibrations  
 at Surfaces V Conference (September 1987).  
 Member, Board of Trustee's Visiting Committee for the College of Arts  
 and Science, University of Rochester (July 1, 1987 - June 30, 1993).  
 Member, Council of the University Senate, The University of Chicago  
 (September 1989 - September 1992).  
 Member, IQEC '90 Program Committee (May 1990).  
 Member, Physical Electronics Conference Advisory Committee (1991).  
 Member, Physical Electronics Conference Committee (1991-1994).  
 Organizer, Symposium on "Surface Chemistry from Reaction Dynamics  
 Through Materials Growth", August 1992, ACS National Meeting,  
 Washington, DC.  
 Co-Chairman, Symposium on "Laser Techniques for Surface Science",  
 January 1994, SPIE/OE LASE '94, Los Angeles, CA.  
 Chairman, ACS Irving Langmuir Prize Canvassing Committee (1995).  
 Division of Chemical Physics, American Physical Society:  
 Vice-Chair (1994), Chair-Elect (1995).

**Research Interests**

Surface Chemistry & Physics; Interfacial Kinetic Processes; Chemical  
 Physics; Reaction Dynamics; Electrochemistry; Materials Growth and  
 Thin Film Dynamics; Molecular Beam Scattering; Surface Metallurgy;  
 interface oxidation, vibrational dynamics, alloys, phase transitions;  
 Nanostructures; STM/AFM studies of surface phenomena.

**End Document**